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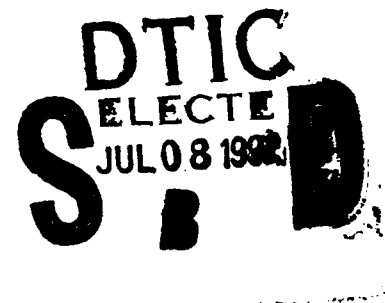
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LASER INDUCED FLUORESCENCE DETECTION OF GUMS IN JET FUELS

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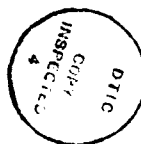
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EXECUTIVE SUMMARY

The current method (ASTM D 381) of determining the concentration of gums in jet fuels is a lengthy procedure requiring a large sample size. Because gum formation is believed to be an important step in the formation of deposits in fuel systems used in jet aircraft, a non-intrusive method of performing spatially resolved measurements of gum concentration in high temperature flow systems is a desired research tool. The present study was conducted to determine the feasibility of using laser-induced fluorescence (LIF) to monitor gum concentration in jet fuel.

Fourteen test fuels were oxidatively stressed at 100 °C using an initial oxygen pressure of 100 psig. Several oxidation parameters including induction period, breakpoint, soluble and insoluble gums, oxidation rate, gum-oxygen ratio, and the solubility of oxygen in the test fuels were determined. Samples of soluble gums and insoluble gums formed from each test fuel were examined with LIF.

Laser-induced fluorescence measurements were performed according to standard laboratory procedures using the 488-nm excitation line from a continuous-wave argon-ion laser. Fluorescence was measured normal to the excitation source with a Jarrell-Ash 0.275-m spectrometer equipped with an EG&G/PAR optical multichannel analyzer (OMA) system.

The LIF spectra of the gums from the various test fuels were similar in that they occurred within the same spectral window (500 to 750 nm). However, there were variations in the half intensity widths of the spectra that should be addressed in future attempts to measure the fluorescence intensity of gums. An argon-ion laser was found to be a good excitation source for LIF of gums in jet fuels. Other excitation sources in the ultraviolet at 325 nm and the red at 635.1 nm were not effective in the LIF detection of gums in jet fuels.

The results of the study showed a correlation between LIF and the gum content of jet fuels. However, the LIF intensity was not always a simple linear function of the gum concentration. A detailed examination of the effect of gum concentration on LIF was performed for only two of the test fuels so it is unknown whether or not the correlation of LIF intensity with gum concentration would be the same for all jet fuels. Among the test fuels examined, two of the fuels showed a negative correlation between LIF intensity and

gum concentration. It appeared that those fuels, which gave negative correlations, contained fluorophores that interfered with the fluorescence from gums.

The results indicated that gum aging had a significant influence on the relationship between LIF intensity and gum concentration. It was concluded that gums undergo significant changes in molecular structure for a period well after their inception.

The responsivity of LIF to gums varied with fuel specification and composition. The term "responsivity" is used to describe in relative units, the fluorescence intensity that is emitted per unit of gum concentration in the test fuels. It appeared to depend partly on the rate at which gums were formed in the test fuels. Extreme variations in responsivity seemed to be related to gum aging. Changing responsivity is a factor that complicates the use of LIF in making an absolute measurement of soluble gums in jet fuels. To perform a gum concentration measurement, the technique requires a calibration procedure for each jet fuel tested.

Experiments on fluorescence quenching by molecular oxygen showed that this effect did not interfere with the LIF detection of gums in jet fuels. Preliminary LIF measurements show relatively weak fluorescence from fuel additives. It was concluded that fluorescence from fuel additives should not interfere with the LIF detection of gums in jet fuels.

This study has revealed several effects, such as gum aging and the interference of other fluorophores with gum-fluorescence, which require further investigation before LIF is to be considered a quantitative technique for measuring gums in jet fuels. However, this study has shown that the formation of gums in jet fuels is detectable by LIF. The results of this study show that gum formation in some fuels correlates strongly with LIF while for other fuels the results are ambiguous. In other words, if the test fuel is selected carefully, there is a high probability that gum formation will correlate with LIF. On that basis, the present study indicates that LIF could become a very useful research technique for making spatially-resolved nonintrusive qualitative-measurements of gums in experiments on jet fuel stability and deposit formation.

INTRODUCTION

The mechanism of the formation of deposits from jet fuels is a complex process involving several chemical reactions, mass transport effects and surface interactions. In the most general case, deposits form as the result of fuel oxidation, of which the first step in the mechanism is the formation of peroxides. The thermal decomposition of peroxides and the ensuing free radical chain reactions lead to the formation of several oxygenated compounds and higher molecular weight species known as gums. Gums have molecular weights ranging from 2 to 4 times that of the average fuel molecule. They are very rich in oxygen and often contain significant amounts of sulfur and nitrogen which are present in only trace quantities in the neat fuel. Because of their relatively high heteroatom content, gums have only limited solubility in the fuel. For that reason, gums are characterized as soluble and insoluble. In other words, when a fuel is oxidatively stressed, some of the gum formed remains dissolved in the fuel while another portion of it is found as a precipitate. It is the belief held by many researchers that the gums formed by the oxidative stressing process are, in fact, the precursors to deposit formation.

While deposit formation is intrinsically related to fuel oxidation chemistry, it is also affected by other parameters such as the flow conditions, mass transport and surface activity. To determine the thermal stability of a fuel, it is necessary to isolate the effects of fuel oxidation chemistry from the other aspects of the deposition mechanism. Since gums appear to be the critical product of fuel oxidation, it has been suggested that the effect of chemistry in the deposition mechanism could be manifested as a global rate constant for the formation of gums. To determine the global rate constant for the formation of gums in fuels, it is necessary to measure their rate of formation. However, the actual measurement of the rate of formation of gums hinges upon the current capability to measure gum concentration in jet fuels.

Currently, the ASTM D 381 method using the steam jet evaporation technique is the only established method of measuring the concentration of gums in jet fuels. The basic problems of large sample size, 100 mL, lengthy analysis, ≈ 2 hrs, poor accuracy, and its intrusiveness tend to discourage the use of the D 381 method in studies of the kinetics of gum formation in jet fuels.

In view of the difficulties in measuring gums in jet fuels, other methods of analysis have been explored at Southwest Research Institute (SwRI). In the examination of fuels that contain gums, it has been found that the gums seem to always cause the fuel to have a slight brandy color which is characteristic of light absorption in the blue, ≈ 450 nm, region of the spectrum. The absorption spectrum of gums dissolved in fuel was found to be a broad band continuum beginning at about 550 nm and increasing in intensity monotonically into the blue and violet regions of the spectrum. For a pristine hydrocarbon fuel there is little or no light absorption in the visible region of the spectrum. However, gums formed by oxidatively stressing the fuel appear to have a significant absorption in the 450-nm region of the spectrum where the neat fuel is essentially transparent. In light of these observations, it became apparent that a spectroscopic method such as laser-induced fluorescence (LIF) could be used to measure gums in jet fuels.

BACKGROUND

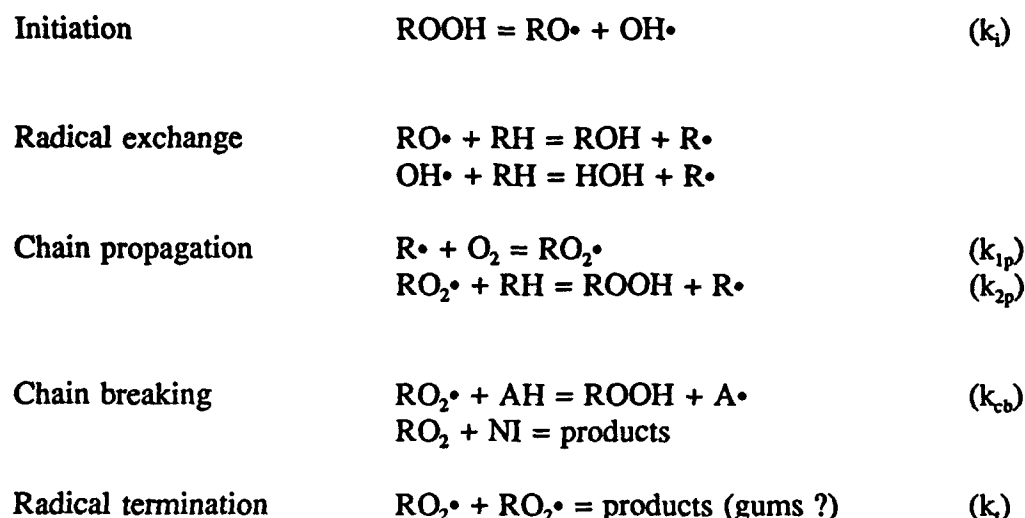
The formation of deposits from jet fuels is a complex process involving several reaction steps. It is generally accepted that most deposits from jet fuels are formed from the products of autoxidation. The process begins with the formation of alkyl hydroperoxides. The thermal decomposition of the peroxides into free radicals, and the ensuing chain propagation reactions lead to the formation of several oxygenated compounds including some species with molecular weights a little more than two to three times that of the average fuel molecule. These higher molecular weight species, commonly known as gums, contain relatively high concentrations of oxygen, sulfur, and nitrogen, and are only partially soluble in the fuel.

When jet fuels are autoxidized, the trace amounts of sulfur and nitrogen in the fuel tend to concentrate in the gum molecules. It is believed that the hydrocarbons that contain heteroatoms become part of the gum because they act as natural autoxidation inhibitors and thus are intimately involved in the oxidation process.

Autoxidation

The autoxidation of jet fuels is based on a free-radical mechanism⁽¹⁻⁹⁾, which includes the familiar radical initiation, propagation, chain breaking, and termination reaction steps. While several relatively complex reaction steps are conceivable in the overall autoxidation

of hydrocarbon fuels, the formation of alkyl hydroperoxides, ROOH, and the role of the inhibitors such as antioxidants, AH, may be described succinctly by the following mechanism:



where AH is a synthetic antioxidant, NI is a natural oxidation inhibitor, $\text{RO}\cdot$, $\text{OH}\cdot$, $\text{R}\cdot$, $\text{RO}_2\cdot$, and $\text{A}\cdot$ are free radicals species, and k_i is the rate constant for initiation, etc.

In this mechanism, the alkyl hydroperoxide, ROOH, itself, is the radical initiator⁽¹⁻⁴⁾. For a truly pristine fuel, autoxidation would be nearly nonexistent if it were not for a trace of radical initiator such as ROOH. In reality, all fuels contain a trace of ROOH because oxygen is ubiquitous, and free radicals are formed by natural radiation sources such as muons.

The radical exchange reactions rapidly convert the radicals, $\text{HO}\cdot$ and $\text{RO}\cdot$ formed in the initiation step to alkyl radicals, $\text{R}\cdot$. Alkyl radicals, $\text{R}\cdot$, react very fast with oxygen to form alkylperoxyl radicals, $\text{RO}_2\cdot$. The Reaction 1p takes place on almost every molecular collision because it is basically a radical recombination reaction with little or no activation energy. Therefore, Reaction 1p is highly preferred over the reaction, $\text{R}\cdot + \text{AH} = \text{RH} + \text{A}\cdot$, which has a relatively high activation energy. Also, since the concentration of $\text{R}\cdot$ is very low compared to the alkylperoxyl radical, $\text{RO}_2\cdot$, it has even less of an opportunity to react with the antioxidant AH. $\text{RO}_2\cdot$ tends to build up in the system, and comprises the main radical pool, because it has few reaction partners other than RH and AH. Recall that Reactions 2p

and cb are much slower than Reaction 1p. Because the A-H bond energy in an antioxidant such as a hindered phenol is significantly less than that of R-H, the activation energy of Reaction cb is less than that of 2p. Consequently, $RO_2\cdot$ is more rapidly consumed by AH, which explains why the antioxidant depletes the radical pool and slows down the oxidation process. The natural inhibitor, NI, is also believed to deplete the radical pool, but it may inhibit the oxidation reaction by a different reaction mechanism.

In the absence of oxidation inhibitors the radicals are terminated principally by the recombination of $RO_2\cdot$ radicals. Therefore, by neglecting the chain breaking reactions and making the steady-state approximation for the free-radical concentrations, $[HO\cdot]$, $[RO\cdot]$, $[R\cdot]$, and $[RO_2\cdot]$, the following expression may be derived relating the peroxide concentration, $[ROOH]$, and the oxidation time, τ .

$$\sqrt{[ROOH]} = k_{2p} \sqrt{\frac{k_1}{2k_t}} [RH] \tau \quad (1)$$

According to Eqn. 1 the rate of formation of peroxides is independent of the oxygen concentration and depends only on the hydrocarbon concentration, which remains essentially constant during the autoxidation process. It is important to note⁽⁵⁾ that the autoxidation rate could become dependent on oxygen concentration, if the partial pressure of oxygen is too low (e.g., ≈ 0.138 psia). In the present study the oxygen pressure in the reactor used to stress the fuel was 100 psia, so the autoxidation rate was independent of oxygen concentration.

Oxidation Inhibitors

The autoxidation of jet fuels usually proceeds very slowly at first and then at some later date breaks into a relatively fast oxidation reaction. The slow oxidation process is termed the induction period and the rapid oxidation is called the post-induction reaction. The term, breakpoint, is often used to denote the end of the induction period or the beginning of the post-induction reaction. Figure 1 shows typical correlations of the peroxide buildup versus time, based on Eqn. 1, for the autoxidation of a jet fuel. Note that an induction period is observed in the autoxidation of the neat fuel. When an antioxidant is added to the fuel, the induction period increases; the length of the induction period appears to be roughly proportional to the amount of antioxidant that is added to the fuel.

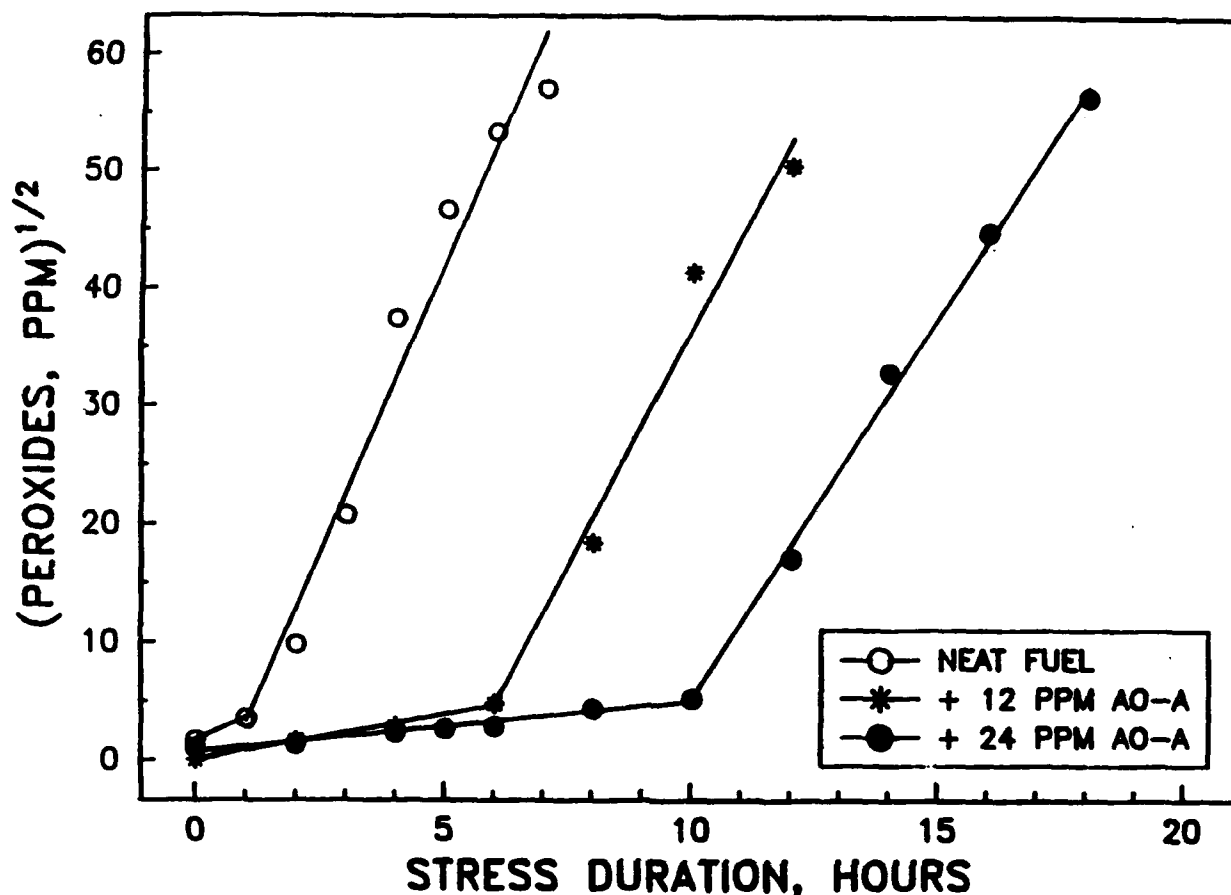


Figure 1. The effect of an antioxidant on the formation of peroxides in a jet fuel. The autoxidation reaction was performed in a stirred reactor at 100 °C with an oxygen pressure of 20 psig. The slight increase in peroxide formation is the induction period. The discrete increase in the formation of peroxides marks the breakpoint and the beginning of the post-induction time.

Induction periods are observed in the oxidations of most jet fuels. However, sometimes the autoxidations of jet fuels, and more often pure hydrocarbons, exhibit little or no induction period. While the concept of an induction period is not completely understood, it is generally believed that it is caused by naturally occurring oxidation inhibitors in the fuel. This conclusion is based on the observation that when antioxidants are added to a jet fuel, the induction period is extended and the rate of autoxidation is substantially reduced. It appears that the antioxidant is depleted at the end of the induction period because there is no effect on the rate of the post-induction. As mentioned above, the results shown in Figure 1

indicate that the length of the induction period is roughly proportional to the amount of the antioxidant added to the fuel. This is explained in the following analysis.

For fuels containing antioxidants, the radical termination process is dominated by Reaction cb so $k_{cb}[RO_2][AH] \gg k_t[RO_2]^2$. If the natural inhibitors in the fuel have been consumed, i.e., $[NI] = 0$, and the steady-state approximation is used for all radicals including RO_2^\bullet , it may be shown that

$$k_{cb}[RO_2][AH] = 2k_i[ROOH] \quad (2)$$

Assuming that AH is consumed only in Reaction, cb, it follows that

$$\frac{d[AH]}{dt} = -k_{cb}[RO_2][AH] \quad (3)$$

so by combining Eqns. 2 and 3, the induction period, τ_{IP} , may be expressed as

$$\tau_{IP} = \frac{[AH]_0}{2k_i[ROOH]_{\tau_{IP}}} \quad (4)$$

where $[AH]_0$ is the initial concentration of antioxidant and $[ROOH]_{\tau_{IP}}$ is the concentration of peroxide in the fuel at the end of the induction period. Equation 4 indicates that τ_{IP} is proportional to the initial concentration of antioxidant in the fuel, which roughly agrees with the results shown in Figure 1. Any slight departure from Eqn. 4 may be caused by subsequent reactions of the antioxidant radical, A, with O_2 and RH. These reactions were not included in the steady state equations used to derive Eqn. 4. As the antioxidant radicals, A, build up in the fuel, they are expected to have a greater influence on the steady-state concentration of RO_2 radicals. It may be that the efficiency of an antioxidant depends more so on the reactivity of the radical, A, than on the rate of Reaction, cb. This may explain why some antioxidants are more effective than others.

Gums and Deposits

It is the belief held by most workers, e.g., strongly supported by the works of Mayo and Lan⁽¹⁰⁻¹²⁾, that the gums are the precursors to deposit formation. Although deposit

formation depends on parameters^(13,14) other than chemistry such as the flow conditions, mass transport and surface activity, thermal stability still seems to be most indicated by the fuels tendency to form gums. This is why a global rate constant for the formation of gums could be an immensely versatile fuel property for predicting the potential deposit formation in aircraft fuel systems at specified temperature and flow conditions.

To determine the global rate constant for the formation of insolubles in fuels, the rate of gum formation needs to be measured under controlled conditions, specifically, constant temperature. However, the actual measurement of the rate of formation of gums hinges upon the current capability to measure gum concentration in jet fuels. Currently, the ASTM D 381 method using the steam jet evaporation technique is the only established method of measuring the concentration of gums in jet fuels. The basic problems with the D 381 method, which include large sample size, 100 mL, lengthy analysis, ≈ 2 hrs, poor accuracy, and intrusiveness, tend to discourage its use in examining the kinetics of gums and deposit formation in jet fuels.

Other methods of gum analysis have been reported, but they too appear to fall short of providing a high response, non-intrusive analysis. Mayo and Lan⁽¹²⁾ report favorable results on a modified D 381 gum analysis scheme that only requires a fuel sample of only 4 mL. The sensitivity of the modified D 381 method appears to be compromised by the small volume of the fuel sample; however, Mayo and Lan claimed that the 25-to-1 reduction in fuel sample size can be compensated for by an improved weighing technique.

Cheng et al.⁽¹⁵⁾ used ultraviolet absorption spectroscopy to quantifying gum content in fuels. Their measurements, which were performed on one fuel, were based on the difference between the ultraviolet absorption (300 to 360 nm) spectra of a pristine fuel and the same fuel that had been thermally stressed. That is, the measurement was performed with the pristine fuel in the reference cell and the stressed fuel in the sample cell of the spectrophotometer. Several attempts to repeat the experiment of Cheng et al.⁽¹⁵⁾ using fuel samples available at SwRI have failed. It appears that the method is strongly dependent on the ultraviolet absorption spectrum of the fuel and it seems that Cheng et al.⁽¹⁵⁾ performed their experiments on a fuel that exhibited relatively low ultraviolet interference in the region of the spectrum where the gums strongly absorbed.

In view of the difficulties in measuring gums in jet fuels, other spectroscopic methods of analysis have been explored at SwRI. In the examination of fuels that contain gums, it has been found that the gums seem to always cause the fuel to have a slight brandy color that is characteristic of light absorption in the blue region of the visible spectrum. Similar observations have been reported by others such as the work by Bhan et al.⁽¹⁶⁾ which suggests that there is a correlation between color change and sediment formation in marine diesel fuels.

The fact that jet fuels are relatively transparent to light in the visible region of the spectrum, whereas gums exhibit a finite absorption there, indicates that gums could be detected spectroscopically. The first method that came to mind was simply to use light absorption in the blue region (ca. 450 nm) of the spectrum as mentioned above. Light absorption appeared to work in principle, but it did not have the sensitivity required to support the development of a practical method of detecting gums in jet fuels.

In a search for more sensitive methods of measuring gums at SwRI, laser diagnostic techniques were considered. The realization that gums absorb light in the visible region of the spectrum where fuels are otherwise transparent, invited the thought that light absorption by gums could give rise to fluorescence.

Laser-Induced Luminescence (LIL)

Laser-induced luminescence is a relatively new spectroscopic technique for making spatially resolved concentrations measurements of both stable and short lived species in difficult to examine environments such as flames and plasmas (17,18). In principle, LIL is emission of light resulting from absorption of laser energy by a substance. Reradiated light contains a major component at the wavelength of the exciting laser light (reflected light); however, there are also many new wavelengths (luminescence) that are determined primarily by the electronic structure of the substance.

Figure 2 shows a typical energy level diagram for an atom. Among the three energy levels shown in the diagram, the lowest lying one is termed the ground state and the others, A and B, are excited states. When light is absorbed by an atom in its ground state, the atom makes a transition to the excited A state. From the excited A state, some of the atoms will fall back to the ground state and emit light with the same wavelength that was absorbed (Re-

emitted or Resonance Fluorescence), and some will make a transition to the intermediate B state and emit light with a different wavelength. This new fluorescence of a different wavelength is useful in identifying and characterizing a substance because it depends on the atomic or molecular structure of the substance. Laser-induced luminescence includes both laser-induced fluorescence (LIF), which is fast luminescence occurring on time scales of the order of several nanoseconds, and laser-induced phosphorescence (LIP), which is slower luminescence occurring on time scales as long as several seconds. The luminescence spectrum is not only a function of time, but also a function of the excitation spectrum.

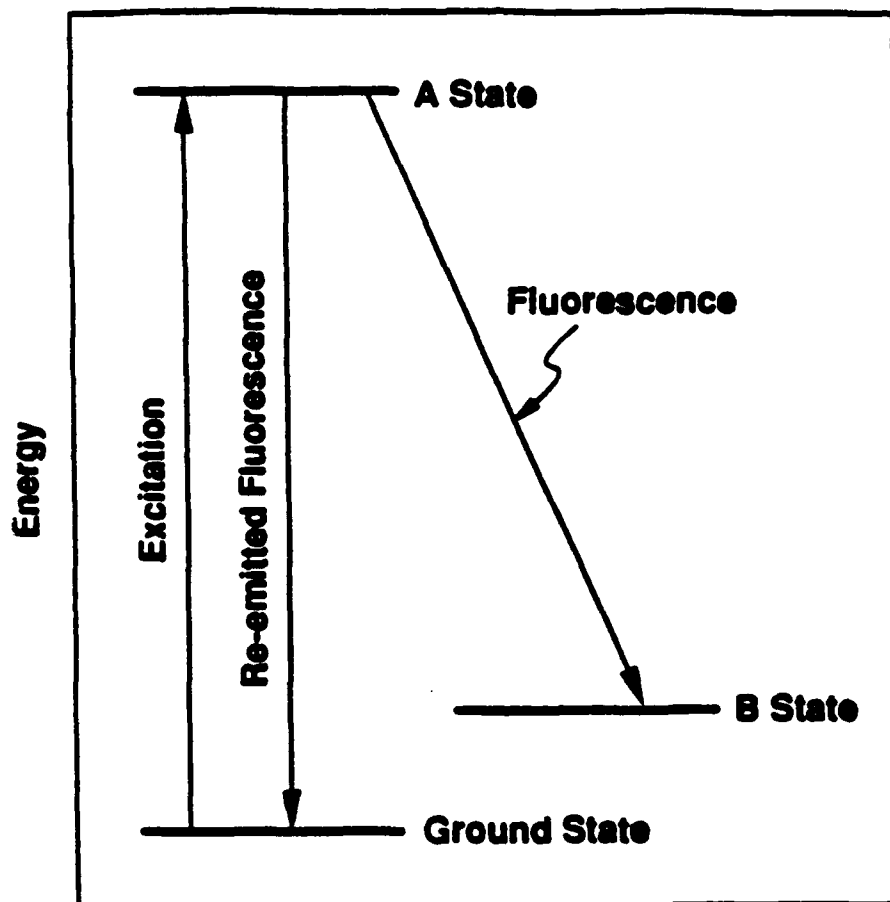


Figure 2. Energy level diagram for an atom or a molecule

Fluorescence and phosphorescence have been studied for a number of years and have been used in numerous ways in the laboratory environment. Laser-induced luminescence is finding widespread use in many new and diverse applications; for example, it is currently being used to study energy redistribution collisions in vapors, for fingerprint detection, and

to map flow fields in chemical lasers. In recent years, advances in laser technology have increased reliability and portability of lasers and also generally reduced costs; this is readily demonstrated by the wide use of helium-neon lasers in bar-code scanners found in many supermarkets.

In many applications, fluorescence dominates phosphorescence. Fluorescence is characterized by many spectra depending on the excitation wavelength. A fluorescent molecule emits a fluorescence spectrum after it absorbs radiation within its excitation spectrum. The spectral distribution of the fluorescent radiation is a physical and absolute characteristic of a given substance for a given excitation wavelength and is useful for qualitative considerations. Emission intensity of fluorescence at a given wavelength is useful for quantitative analysis with a given instrument after standardization. Quantitative measurements show that there is sometimes a very strong correlation between laser-induced luminescence and some physical characteristic of the material; many times this is because fluorescence primarily reveals relationships between molecular functional groups, such as conjugation. Because relationships between certain molecular functional groups are altered during degradation, laser-induced luminescence can be used to monitor these processes.

With the monochromaticity and power density available from lasers, transitions can be probed in molecules that are not normally thought of as fluorescent. For instance, fluorophores that exhibit ultraviolet absorption can sometimes be induced to fluoresce with laser excitation in the visible region of the spectrum. This effect can be very important from the viewpoint of practical implementation.

When laser-induced fluorescence is measured or visually assessed using optical filters instead of a narrow-bandwidth spectrometer, fluorescence signals of several wavelengths are measured simultaneously. Laser-induced fluorescence measured in this fashion is referred to as "integrated fluorescence" because the signal is related to the integral of the fluorescent-light intensity, weighted by the filter-detector response, over the wavelengths to which the system responds. Hence,

$$I(\lambda_e) = \int LIF(\lambda_e, \lambda) D(\lambda) F(\lambda) d\lambda \quad (5)$$

$I(\lambda_e)$ = integrated fluorescence for excitation wavelength λ_e ,

$LIF(\lambda_e, \lambda)$ = laser-induced fluorescence at wavelength λ when excited with wavelength λ_e ,

$D(\lambda)$ = detector response at wavelength λ ,

$f(\lambda)$ = filter response at wavelength λ .

Note that $LIF(\lambda_e, \lambda)$ is also a function of the penetration depths (absorption and scattering parameters) for both the excitation and detection wavelengths, as well as the quantum yield for fluorescence of the material.

LIL From Gums

Preliminary experiments using a Turner model 430 spectrofluorometer showed that there was a distinct fluorescence at about 550 nm from a solution of acetonitrile containing about 80 mg/dL of gum. The fluorescence appeared to be most intense when the incident xenon lamp light source was blue (ca. 450 nm). However, the fluorescence was weak and required the most sensitive scale of the instrument to obtain a reasonable spectrum.

In principle, the intensity of fluorescence increases in proportion to the incident light intensity. Because laser light sources are several orders of magnitude more intense than a dispersed xenon lamp, the laser-induced fluorescence (LIF) signal is also proportionately stronger. Replacing the xenon lamp with an Argon-Ion laser emitting at 488 nm produced very strong fluorescence from the acetonitrile solution containing 80 mg/dL of gum. The experiment was then repeated using a sample of oxidatively stressed fuel which contained some gum. It was found that the presence of gum in the fuel gave rise to a dramatic increase in the fluorescence intensity. These preliminary results were very encouraging and indicated a high probability of success in the development of an LIF technique for measuring gum in jet fuels.

OBJECTIVE

The purpose of the study is to investigate the feasibility of using laser-induced fluorescence (LIF) to measure soluble gums in jet fuels.

EXPERIMENTAL APPROACH

A comprehensive approach including fuel technology and laser diagnostics was required to meet the objective of the project. To access the feasibility of using LIF to measure gums in jet fuels, it was necessary to determine, 1) if the fluorescence spectra of gums are dependent on fuel properties and specifications, 2) if the LIF intensity is a linear function of the gum concentration, and 3) the effect of the wavelength of the incident laser light source on the LIF intensity?

General

To investigate the feasibility of measuring gums by LIF, it was necessary to produce gums from a wide variety of fuels. Gum samples were prepared by oxidatively stressing fourteen test fuels which ranged from JP-4 to JP-7 and were derived from different sources including petroleum, shale oil, and coal. The fuels were oxidatively stressed in a static reactor at 100 °C beginning with an initial oxygen pressure of 100 psig. The oxygen pressure was monitored to follow the progress of the autoxidation process. Measurements included the breakpoint, oxygen consumption, both soluble and insoluble gums, and the peroxide content of the stressed fuel. The ASTM methods D 381 and D 3703 were used respectively to analyze the gums and the peroxide content of the stressed fuel.

The LIF spectra of both soluble and insoluble gums were obtained for each test fuel. The results were examined to determine similarities in the spectra, the responsivity and the dependence of the fluorescence intensity on the concentration of gums in the stressed fuels. The soluble gum samples from the stressed fuels were diluted with different amounts of the neat fuel to determine the linearity of the LIF response versus the gum concentration. Two of the test fuels were oxidatively stressed at several durations to produce fuel samples with a wide range of gum concentrations.

Oxidative Stressing

Oxidative stressing of the test fuels was performed using a modified version of the ASTM D 525 thermal stability test procedure for measuring breakpoint. The tests were performed in high pressure stainless steel oxidation bombs equipped with glass liners. The glass liner was filled with 100 mL of fuel and sealed in the bomb. The bomb was purged

with pure oxygen and then pressurized with 100 psig of pure oxygen. The initial pressure, measured with a Wallace and Tiernan Gage, was recorded immediately after the bomb was pressurized. The bomb was then allowed to stand at room temperature for about 3 hours or until the pressure equilibrated. Note that when oxygen is initially placed in the bomb, there is little or no oxygen dissolved in the fuel. Once the bomb is filled with oxygen and sealed, the oxygen pressure drops about 20 psi due to dissolution of oxygen in the fuel. For several of the test fuels, the exact pressure drop was recorded so it would be possible to calculate the Henry's law constant for the solubility of oxygen in the fuel.

After the oxygen pressure equilibrates, the bomb is placed in a steam bath at approximately 100 °C. The pressure is monitored continuously with a circular pressure meter and frequent pressure readings are taken from the Wallace and Tiernan gage. During the early stages of the autoxidation process, there is an induction period which is observed as a very slow rate of decrease in the oxygen pressure in the bomb. During the induction period the pressure decreases about 10 to 15 psi and the peroxide concentration in the fuel reaches about 100 ppm. The end of the induction period (breakpoint) is followed by a relatively rapid decrease in the oxygen pressure. During this post-induction reaction, there is a substantial increase in the formation of peroxides and gums. In experiments to generate gum samples for LIF studies, the post-induction time was varied to produce the desired gum concentration.

Test Fuels

Fourteen jet fuels described in Table 1 were used in the study. Most of the test fuels were supplied by Wright-Patterson AFB. In selecting the test fuels, the intention was to find as wide a variety of fuels as possible. It was important to vary both the fuel specification and the composition. As shown in Table 1, the fuels have a relatively broad range of specifications including JP-4, JP-5, JP-7, and JP-8, and are derived from petroleum, shale oil, and coal. The test fuels were stored in a cold box to prevent any change due to oxidative instability during the course of the study.

Table 1. Test Fuels

Fuel Number	Fuel Type	Flash Point, °F	Chemical Description	Sample Size (gal)	Origin
1701	Surrogate JP-8		Blend of pure compounds	1	Petroleum, WPAFB
1702	JP-7	140		5	Petroleum, WPAFB
1703	JP-8	130		5	Petroleum, WPAFB
1704	JP-8	130	Clay Treated	5	Petroleum, WPAFB
1705	JP-5	145		5	Petroleum, NAPC
1722	Jet A-1	140		5	Petroleum, WPAFB
1791	JP-8X	144	30 Percent Aromatics	5	Petroleum, WPAFB
1792	JP-8X	133	45 Percent Aromatics	5	Petroleum, WPAFB
1801	JP-8X	136		5	Shale oil, WPAFB
1802	JP-8X	136		5	Petroleum, WPAFB
1823	JP-8	70		5	Coal, WPAFB
1824	JP-4	-20		5	Shale Oil, WPAFB
1825	JP-8	72		5	Coal, WPAFB
18497	JP-5		Hydro-cracked		Petroleum, NAPC

Additives

The following fuel additives were obtained from Wright-Patterson AFB:

90-POSF-2729 Detergent (Combustible Liquid)
90-POSF-2786 AO1 Dispersant/MD (Combustible Liquid)
90-POSF-2744 Detergent/Dispersant (Combustible Liquid)
90-POSF-2748 "Stabilizer" (Combustible Liquid)
90-POSF-2738 Dispersant (Combustible Liquid)
AO-29 2,6-Di-t-butyl-4-methylphenol, Antioxidant (crystals)

These substances were added to one of the test fuels to determine if they would exhibit fluorescence that could interfere with the LIF measurement of gums in jet fuels.

Laser Diagnostics

The following describes the laboratory apparatus and procedures used to make the experimental laser-induced fluorescence measurements. Figure 3 is a schematic diagram of the instrumentation and the optical arrangement.

Excitation Source

A Spectra Physics model 2025-005 argon-ion laser operating at 488 nm was used as the excitation source. For measurements described in this report, the "constant-light output" mode was utilized so that drifts in output power were negligible. Laser power was nominally set at 100 mW using a Coherent model 210 laser power meter or an Eppley thermopile. (Additional adjustments will be discussed later under the "Calibration Procedures" section.) Laser plasma-discharge lines were removed from the beam with an Edmund Scientific P/N 03907 interference filter with central passband centered at 488 nm. The beam was directed with front-surface turning mirrors so that it entered the sample at a 90° angle with respect to the detection axis. The beam was not focussed and had a spot size approximately 2 mm in diameter where it entered the sample.

While most of the measurements were made using the 488-nm line from the argon-ion laser, other laser lines were also available at wavelengths of 457.9 nm, 476.5 nm, 501.7 nm, and 514.5 nm by rotating the prism in the laser. In addition to the argon-ion laser source,

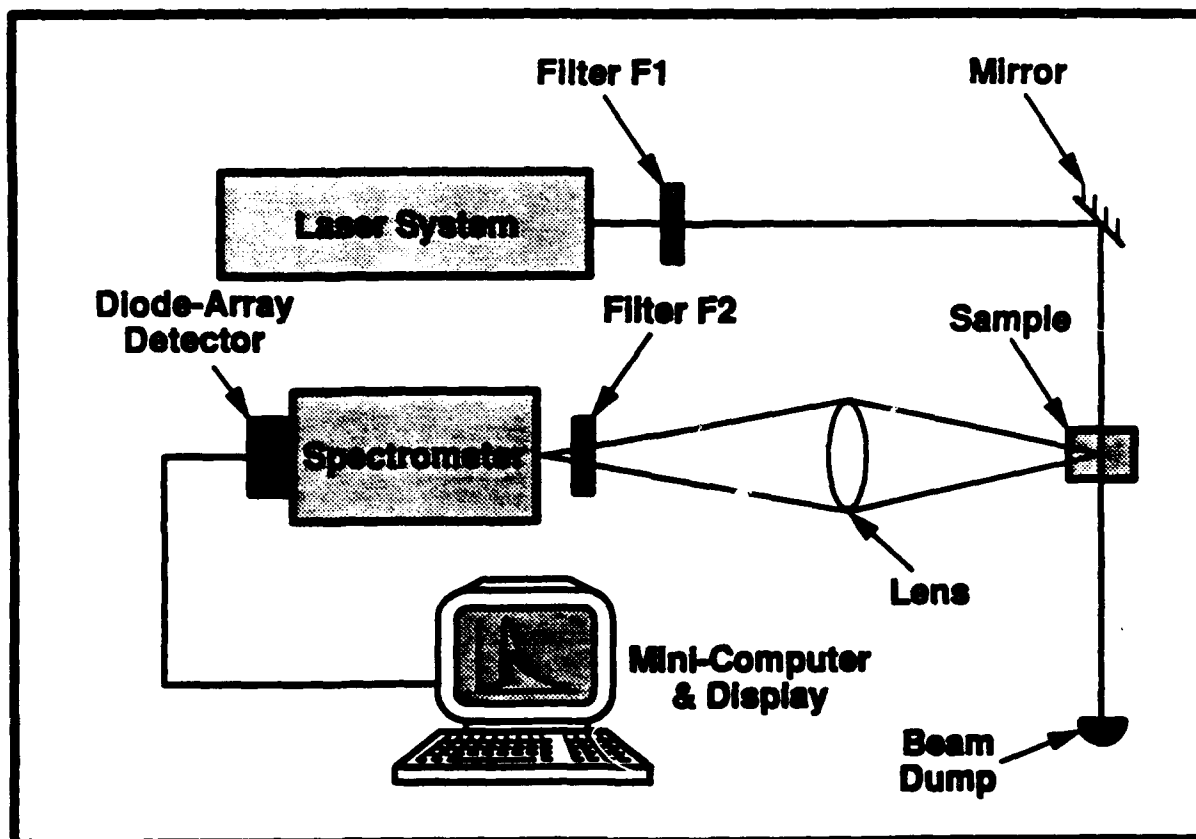


Figure 3. Optical arrangement and instrumentation for laser-induced fluorescence measurements

an Omnicrome model 356 He/Cd laser emitting at 325 nm was used to excite fluorescence in the ultraviolet region of the spectrum, and a Spectra Physics He/Ne laser emitting at 632.8 nm was used to induce fluorescence in the red region of the spectrum.

Sample Containment

Samples were contained in standard fluorescence cuvettes, 10 mm x 10 mm x 45 mm, of either Uvonic type 6H (ultraviolet-grade silica) or 9G (optical glass). Because we were using visible-wavelength excitation in these experiments, it did not matter which cuvettes were used. A cuvette was mounted in place with a shielded cell holder, Oriel P/N 13950, which minimized scattered light from the cell input and output faces; therefore, the clear aperture for the fluorescence measurement was actually reduced to 7 mm in the central portion of the cuvette.

Collection Optics

Light was collected with a simple $f/2.25$ lens arrangement. Scattered laser light was filtered from the fluorescence using a 3-mm-thick piece of Schott OG530 glass. For these measurements, alignment and numerical aperture matching were not critical because the fluorescence was relatively intense. (For most of the jet-fuel samples, fluorescence could be easily seen with the unaided eye when the room lights were turned off.)

Spectrometer System

A Jarrell-Ash 0.275-m spectrometer ($f/3.8$) with a 150-groove/mm grating and a 25-micron-wide slit was used to disperse the light. This is the front-end to an EG&G/PAR optical multichannel analyzer (OMA) system. The detector was a model 1455R-700-HQ microchannel-plate (MCP) intensified diode array. The multi-alkali photocathode has a nominal "S1" response (200-900 nm). It was operated with a Peltier cooler (5°C) and the MCP gain set at 70% of maximum. Typical OMA settings were: 300 msec/scan and 100 scans (averaged). Spectra were digitally stored on 5.25-inch floppy disks for subsequent analysis. The intensity at one point (usually 546.1 nm) was also recorded in a laboratory notebook. Typical spectra show a rapid fall-off of the response at approximately 750 nm and longer wavelengths which was an instrumental artifact caused by physical blockage of the diode array in the present mounting configuration. (Note that the fall-off of response below 530 nm is due to the Schott glass OG530 blocking filter.) Wavelength calibrations were routinely made against a low-pressure mercury discharge.

Calibration Procedures

The system calibration standard for intensity that was used was a Perkin-Elmer #3 fluorescence standard. This is a 3×10^{-3} Molar solution of p-terphenyl in a PMMA plastic matrix which was formed into the same shape as a standard fluorescence cuvette. With 488-nm excitation, this sample gives a fluorescence at 546.1 nm of approximately the same magnitude as the first jet-fuel sample measured. (Note that this standard is traditionally used as a 300-nm ultraviolet-excited dye, which gives intense fluorescence at 340 nm.) The usual procedure was to use this standard to adjust the laser power so that the measured fluorescence at 546.1 nm gave approximately the number of counts comparable to previous measurements. Then the data were normalized by the exact ratio of the two measurements for comparison purposes. A slight problem was found with this procedure in that the fluorescence from the Perkin-Elmer #3 standard would quench slightly if the laser beam was left on it for too long (i.e., 10 minutes). This quenching effect was dealt with by using a routine measurement

technique to minimize the time the standard was in the laser beam. This systematic uncertainty could have introduced an error of approximately $\pm 5\%$ in the fluorescence measurements. In future measurements, a different standard will be used so that this will not occur.

RESULTS AND DISCUSSION

The main purpose of this study was to determine the feasibility of using LIF for measuring soluble gums in jet fuels. However, in the course of performing the study, it was also important to determine as much as possible about the thermal stability properties of the test fuels. This was accomplished in the oxidative stressing experiments which were used to produce the gum samples for the LIF evaluation.

Because jet fuels vary substantially in their rates of autoxidation and in their propensity to form gums, it was important to realize that their thermal stability characteristics may correlate with various aspects of the LIF, such as the intensity of fluorescence per unit mass of gum or possibly the spectral characteristics of the fluorescence. Table 2 gives the results obtained from the oxidative stressing experiments. The fuel stability properties given in Table 2 included the induction period, the post-induction time, the concentrations of soluble gums, insoluble gums, and peroxides, the amount of oxygen consumed, the oxidation rate, and the oxygen-gum ratio. In addition to these measurements, the oxygen solubility constant was determined for several of the test fuels.

Oxidation Rate

Basically, the induction period is the time required to reach the "Breakpoint." During the induction period, very little oxygen is consumed so relatively small amounts of peroxides and gums are produced. At the breakpoint, the rate of oxidation increases dramatically so, from that point on, peroxides and gums are formed rapidly. The oxidation rates were calculated from

$$Rate = \frac{\sqrt{P}}{\Delta t} \quad (7)$$

Table 2. Results of Fuel Stressing Experiments at 100°C

Fuel No.	Induction Time (Hrs)	Post Induction Time (Hrs)	Soluble gums (mg/dL)	Insoluble gums (mg/dL)	Peroxides (ppm)	Oxygen Consumption (mg/dL)	Oxidation Rate (ppm ^{1/2} /hr)	Gain to Oxygen ratio
1701	175	35.5	4.4	2.9	2874	564	1.51	0.013
1702	235	24	15.1	7.3	2004	678	1.87	0.033
1703	379	None	5.8	5.3	3.9	103	0.005*	0.108
1704	355	None	2.7	2.8	7.6	99	0.008*	0.056
1705	648	None	6.2	12.9	16	82	0.006*	0.233
1722	115	57	22.8	10.6	2903	649	0.95	0.051
1791	60	21.7	77.6	24.7	1222	626	1.61	0.163
1791	74	14.7	NA	7.6	1093	517	2.25	---
1792	624	None	59.0	28.0	22.3	144	0.008*	0.602
1792	624	None	57.0	24.0	22.2	169	0.008*	0.490
1801	*	*	17.0	2.4	1180	---	---	---
1801	125	40	100.0	21.2	3010	639	1.37	0.190
1802	385	None	2.0	18.1	15.0	60	0.01*	0.334
1802	385	None	1.8	14.3	14.7	76	0.01*	0.212
1823	57	120	135.3	466.9	125	625	0.093	0.962
1824	119	---	0.9	0.2	227	26	0.13*	0.042
1824	118	50	45.4	14.4	2572	573	1.01	0.104
1825	30	42	198.2	148.2	979	562	0.75	0.617

* Oxygen leaked from reaction bomb.

Oxidation rate based on induction period.

where Δt is the post-induction time and ΔP is the increase in the peroxide concentration in the stressed fuel. In Table 2 the oxidation rate is expressed in units of $\text{ppm}^{1/2}/\text{hr}$. Note that Eqn. 6 is simply another version of Eqn. 1 above. The peroxide concentration was only measured once at the completion of the oxidative stress test, so in determining ΔP , the peroxide concentration was assumed to be about 100 ppm at the breakpoint. In cases where the breakpoint and post-induction time were not observed, the induction time was used to calculate the oxidation rate.

Oxygen Solubility

The oxygen solubility constants for several of the test fuels were determined at room temperature by the procedure mentioned above. The Henry's law constants for solubility were measured in terms of oxygen concentration per unit of oxygen pressure. Typical solubility constants of oxygen in fuel were found to range from 15 to 20 ppm/psi. These values were in good agreement with previous in-house measurements performed at atmospheric conditions using gas chromatography.

Oxygen Consumption

The experiments in the oxidation bomb also yielded information on the amount of oxygen consumed during the oxidative stressing tests. The amount of oxygen consumed was calculated based on measurements of the oxygen pressure change, the oxygen solubility constant and the volume of the vapor space above the fuel in the oxidation bomb. The amount of oxygen consumed was used along with the total gum formed (both soluble and insoluble) to obtain the gum-oxygen ratio given in Table 2. The ratio of gum formed to oxygen consumed is a parameter that has been used by Mayo and Lan⁽¹²⁾ to characterize stabilities of pure compounds, jet fuels, and diesel fuels.

Mayo and Lan found that most pure compounds had relatively low gum-oxygen ratios compared to real middle distillate fuels. Of course, there were a few compounds such as indene and n-methyl pyrole that had exceptionally high gum-oxygen ratios. In their examination of several compounds and fuels, they concluded that fuels that contained substantial proportions of naphthalenes and more condensed aromatic hydrocarbons had the highest gum-oxygen ratios and also had the greatest propensity to form gum. Their conclusions seem to be in good agreement with the present study.

It is evident from the data in Table 2 that the coal derived fuels 1823 and 1825 have relatively high gum-oxygen ratios and the greatest propensity to form gum. Coal derived fuels are rich in polycyclic aromatics and naphthenes. In other words, they contain relatively high concentrations of naphthalenes and condensed aromatic hydrocarbons. On the other hand, Fuel 1701, the surrogate JP-8, has the lowest gum-oxygen ratio. This is probably because Fuel 1701 is composed of several pure compounds. Some of the compounds in Fuel 1701 are particularly reactive, namely methyl naphthalene and tetralin, but their concentrations are not very high (5 percent). The gum-oxygen ratio of Fuel 1702, JP-7, is also significantly lower than the other test fuels. JP-7 is a synthetic fuel with a structure and composition similar to a cyclo-paraffin. Based on the observations of Mayo and Lan⁽¹²⁾, JP-7 would be expected to have a relatively low gum-oxygen ratio. Except for Fuel 1824, which is shale oil derived JP-4, the remaining fuels are petroleum derived. Although their rates of oxidation vary considerably, their gum-oxygen ratios remained in the mid-range of all the fuels tested.

LIF Measurements

There were several goals to be accomplished in making the LIF measurements. It was necessary to determine (1) if significant differences occur in the LIF spectra of the gums formed from the various test fuels, (2) if the spectra of the soluble gums are the same as those of insoluble gums, (3) if the LIF intensity is directly proportional (linear) to the concentration of gum in the fuel, and (4) if the LIF response to gum concentration is the same irrespective of fuel specification and/or composition.

LIF Spectra of Gums

Neat jet fuels fresh from the refiner generally do not exhibit significant fluorescence when radiated with visible 488-nm light from an argon-ion laser. On the other hand, when jet fuels are radiated with ultraviolet light there is a fluorescence in the blue and near ultraviolet regions of the spectrum caused by aromatics and olefins in the fuel. Similarly, jet fuels tend to absorb ultraviolet light very strongly because of the aromatics in the fuel. The fluorescence from ultraviolet light is the basis for the well known ASTM D 1319 determination of aromatics, olefins and saturates in fuels. Fuels that have been oxidatively stressed tend to become partially opaque to visible light. The 488-nm light from an argon-ion

laser causes these oxidatively stressed fuels to fluoresce strongly at wavelengths above 500 nm of the visible spectrum. Because oxidative stressing causes gum formation, it is indicated that the origin of fluorescence induced by the 488-nm excitation is the soluble gum in the fuel.

Figures 4 through 6 show typical spectra of test fuels containing different concentrations of soluble gums. In Figure 4, the spectra of the surrogate JP-8, Fuel 1701, shows a dramatic increase in LIF as the concentration of gums increases. The surrogate JP-8 was a particularly good fuel to examine because it was so very pure and free of fluorophores that would cause a background fluorescence. As a result, there was little or no fluorescence from the control sample. Note that the control was always a neat fuel sample obtained fresh from cold storage. For the real fuels there was always some background fluorescence, but its intensity was usually low compared to that of the oxidatively stressed fuel.

Figure 5 shows LIF spectra of oxidatively stressed Fuel 1791, JP-8X petroleum derived. In comparing the spectra of the surrogate JP-8, Fuel 1701, in Figure 4 with that of Fuel 1791 in Figure 5, it is found that the spectrum of Fuel 1701 is more broad than that from Fuel 1791. The breadth of the spectrum may be related to the variability in the kinds of gum molecules that are formed in the fuel. The surrogate JP-8 was blended with a relatively broad range of hydrocarbons so this variation in composition would also tend to cause a greater diversity in the gums produced. One way to test this speculation would be to examine the LIF spectra of oxidatively stressed pure compounds. They should have relative narrow band spectra. The one important thing to be concluded from these observations is that the spectra of the oxidatively stressed test fuels were similar, but not exactly the same. This will have some bearing on the results that will be presented later in this report.

Except for Fuels 1802 and 1825, the LIF spectral characteristics of the fuels tested were predictable in that they were similar to those of Fuels 1701 and 1791 shown above in Figures 4 and 5. Figure 6 shows that the spectrum of the control sample of Fuel 1825 was more intense and much narrower banded than the oxidatively stressed sample; Fuel 1802 produced a similar result. It is apparent in Figure 6 that the spectrum from the control sample is different than that of the oxidatively stressed sample. Fuels 1802 and 1825 both had some color. Gum was not responsible for the fluorescence from the control sample because a D 381 steam jet analysis of Fuels 1802 and 1825 taken from cold storage showed that they contained little or no gum. It appeared instead, that the controls contained a

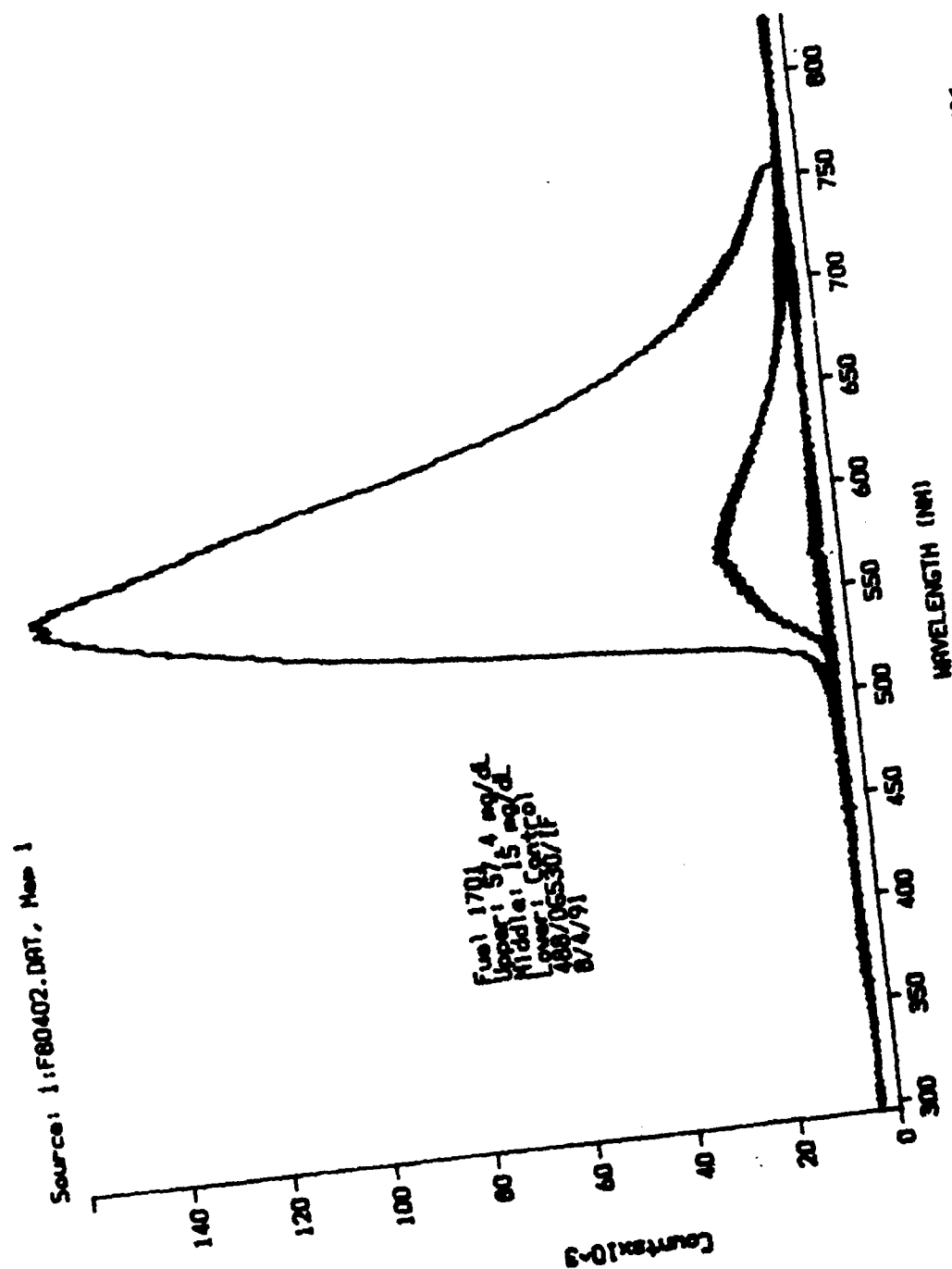


Figure 4. LIF spectra of soluble gums formed from surrogate JP-8, Fuel 1701

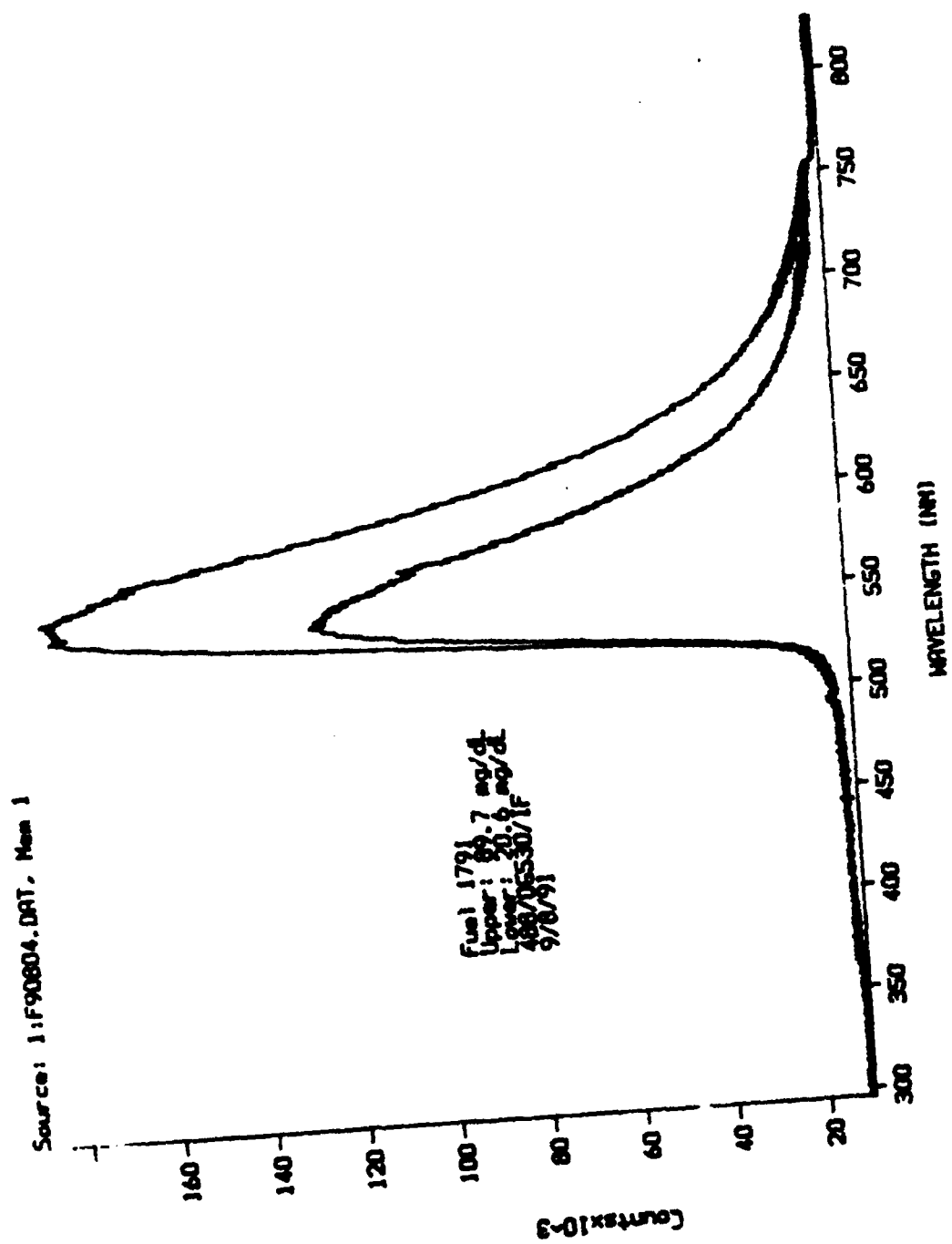


Figure 5. LIF spectra of soluble gums formed from JP-8, Fuel 1791

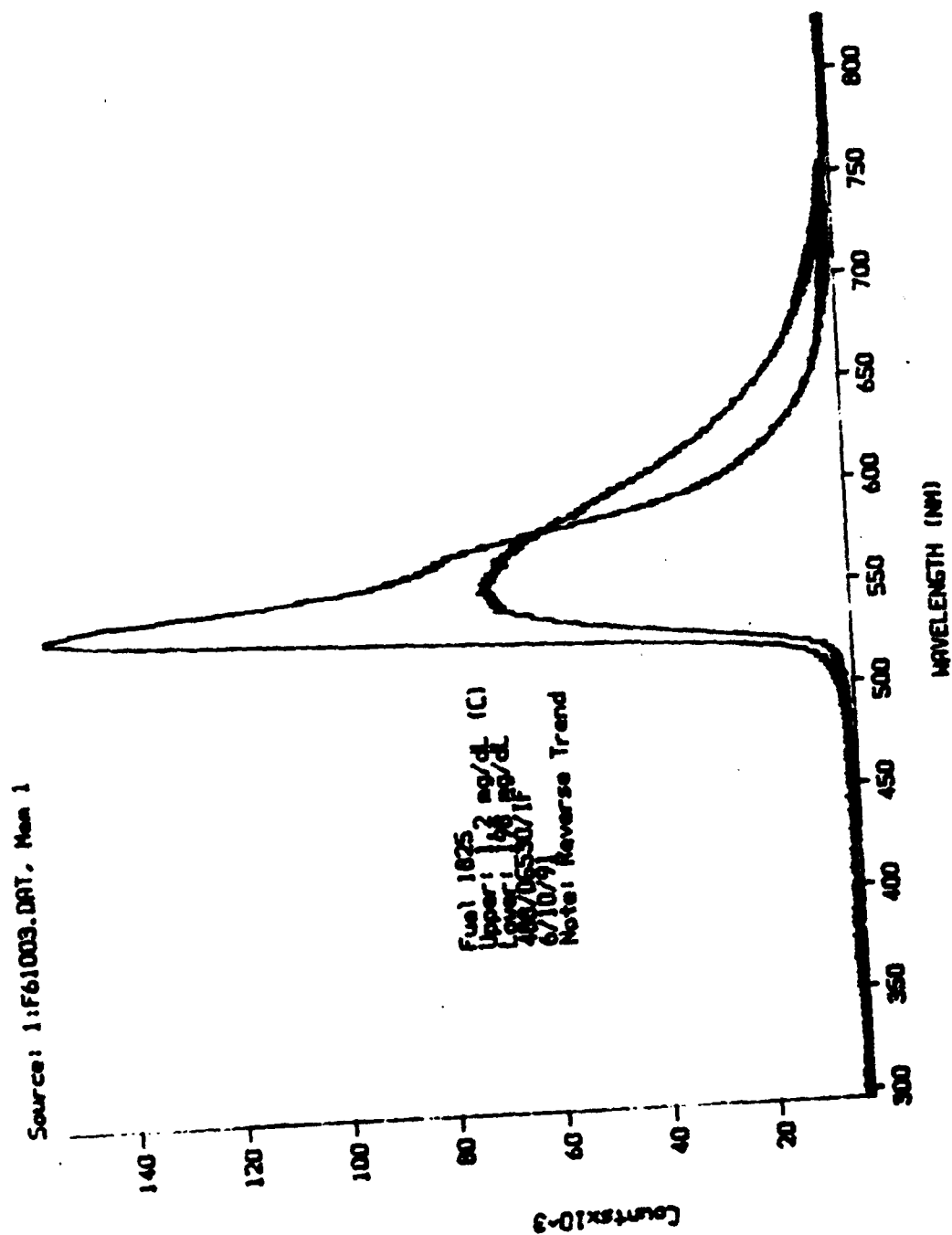


Figure 6. LIF spectra of soluble gums formed from coal derived JP-8, Fuel 1825

fluorescent fluorophore that may have been decomposed or quenched by oxidation products as the fuel was stressed.

The spectrum of the stressed fuel in Figure 6 resembles that of Fuels 1701 and 1791, so it would appear that the fluorescence intensity of stressed fuel is proportional to the gum concentration in that sample.

Soluble vs. Insoluble Gums

LIF measurements were also made on several of the insoluble gum samples obtained from stressing the test fuels. Both soluble and insoluble gums were isolated in the process of performing the steam jet analysis. Known amounts of soluble and insoluble gum were dissolved in TAM to produce two solutions of approximately equal concentration. TAM is a clear solvent composed of toluene, acetone, and methanol that produces zero fluorescence when radiated with 488-nm light from an argon ion laser. Figure 7 shows a comparison of the spectra of soluble and insoluble gums from JP-8 Fuel 18497. The shape of the spectra indicate that soluble and insoluble gums are chemically similar. However, if the peak intensities of the spectra are normalized, it is found that the insoluble gums (lower curve) yield slightly more fluorescence in the red (≈ 700 nm) as compared to the yellow (≈ 560 nm). These subtle differences in spectral shape and the more substantial difference in fluorescence intensities indicate that soluble and insoluble gums may have slightly different molecular structures. Perhaps the spectral differences between soluble and insoluble gums is attributed to their molecular weight difference. It is interesting to note that Mayo and Lan⁽¹²⁾ found soluble gums to consist mostly of dimers whereas insolubles contained more trimers.

Excitation Wavelength Studies

Oxidatively stressed samples of Fuel 18497 and the neat fuel as the control were used in the study to determine the optimum excitation wavelength for LIF detection of gums. Several lasers with different spectral outputs were used in the procedure to determine which excitation would yield the greatest difference between aged fuel and the control. The excitation wavelength sources used in the study included a helium-cadmium laser (325 nm), an argon-ion laser (457.9, 476.5, 488, 501.7, 514.5 nm) and a helium-neon laser (632.8 nm).

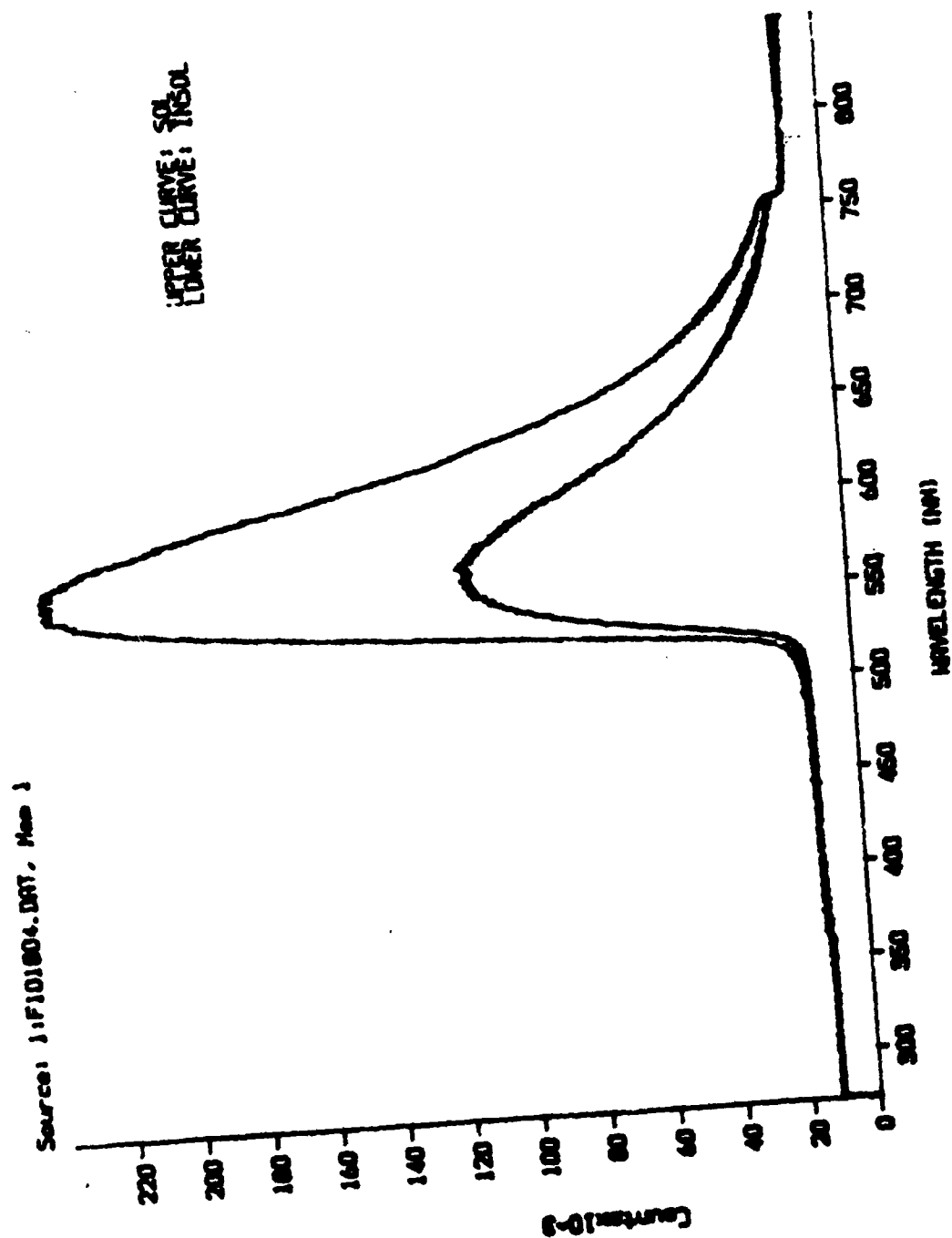


Figure 7. LIF spectra of soluble and insoluble gums formed from Fuel 18497

Figure 8 shows the effect of excitation wavelength on the ratio of the LIF signal from the aged and control fuel samples. The figure shows that the ultraviolet 325-nm excitation caused the control sample to fluoresce more intensely than the aged sample.

With 632.8-nm excitation, fluorescence from both samples was about the same so there was no sensitivity for detecting gums at that wavelength. The greatest difference was observed with the 457.9-nm excitation from the argon-ion laser. For fluorescence observed at 546.1 nm, the ratio of the intensity of the aged sample, LIF(aged), to that of the control sample, LIF(control), i.e., $LIF(aged)/LIF(control)$ was 7.4. All of the argon-ion wavelengths gave ratios greater than 4.0, except for 501.7 nm, which was 2.2. In the present study, the 488-nm line was used as the excitation source because it is one of the strongest and most easily attainable lines produce by the argon-ion laser. The 488-nm line was also chosen because it would be easier for other workers to reproduce the results of the present study.

Gum Aging Studies

The effect of gum aging on the LIF signal intensity was discovered when some of the fuel samples were reexamined about 2 weeks after the initial fluorescence measurements were made. Once this effect was realized, periodic measurements of the LIF intensity were made on several gum samples. Figure 9 shows the effect of LIF intensity on aging of the soluble gum in Fuel 1701 (surrogate JP-8). The figure shows a dramatic increase in the LIF intensity as the fuel sample is aged. Figure 10 shows a similar curve for the effect of aging on the LIF intensity from the insoluble gum formed from Fuel 1701. These fluorescence stressed fuel to that of the control (neat fuel). measurements were performed by dissolving the fuel-insoluble gum in TAM. TAM is a mixture of toluene, acetone, and methanol. In addition to being an excellent solvent for gum, TAM is nonfluorescent with 488-nm excitation.

After examining several of the gum samples for changes in LIF signal intensity with aging, it was found that aging did not effect the LIF intensity of gum samples from the test fuels that oxidized very slowly and did not exhibit a breakpoint in the oxidation bomb. In other words, the test fuels which had indefinite induction periods in the oxidation bomb appeared to produce gums that were more stable. The explanation for this appears to be that the gums were thoroughly aged in the bomb because their residence time there was so much longer than it was for test fuels that formed gums rapidly.

EXCITATION WAVELENGTH STUDY

AL-18497-F 40hrs/100 C

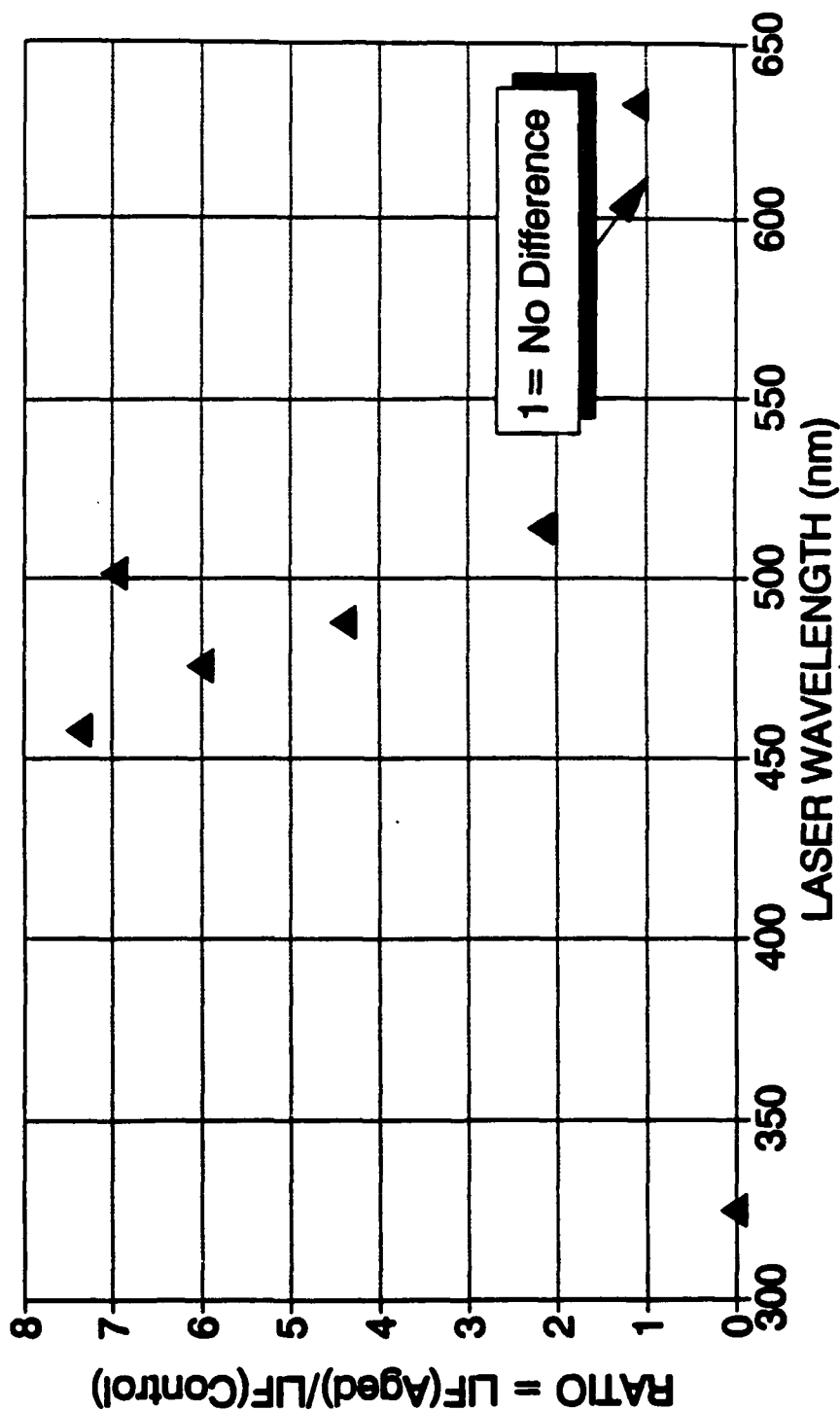


Figure 8. The effect of laser excitation wavelength on the ratio of fluorescence intensity of the stressed fuel to that of the control (neat fuel).

LIF FL-1701-F 488/546.1
FUEL SAMPLES

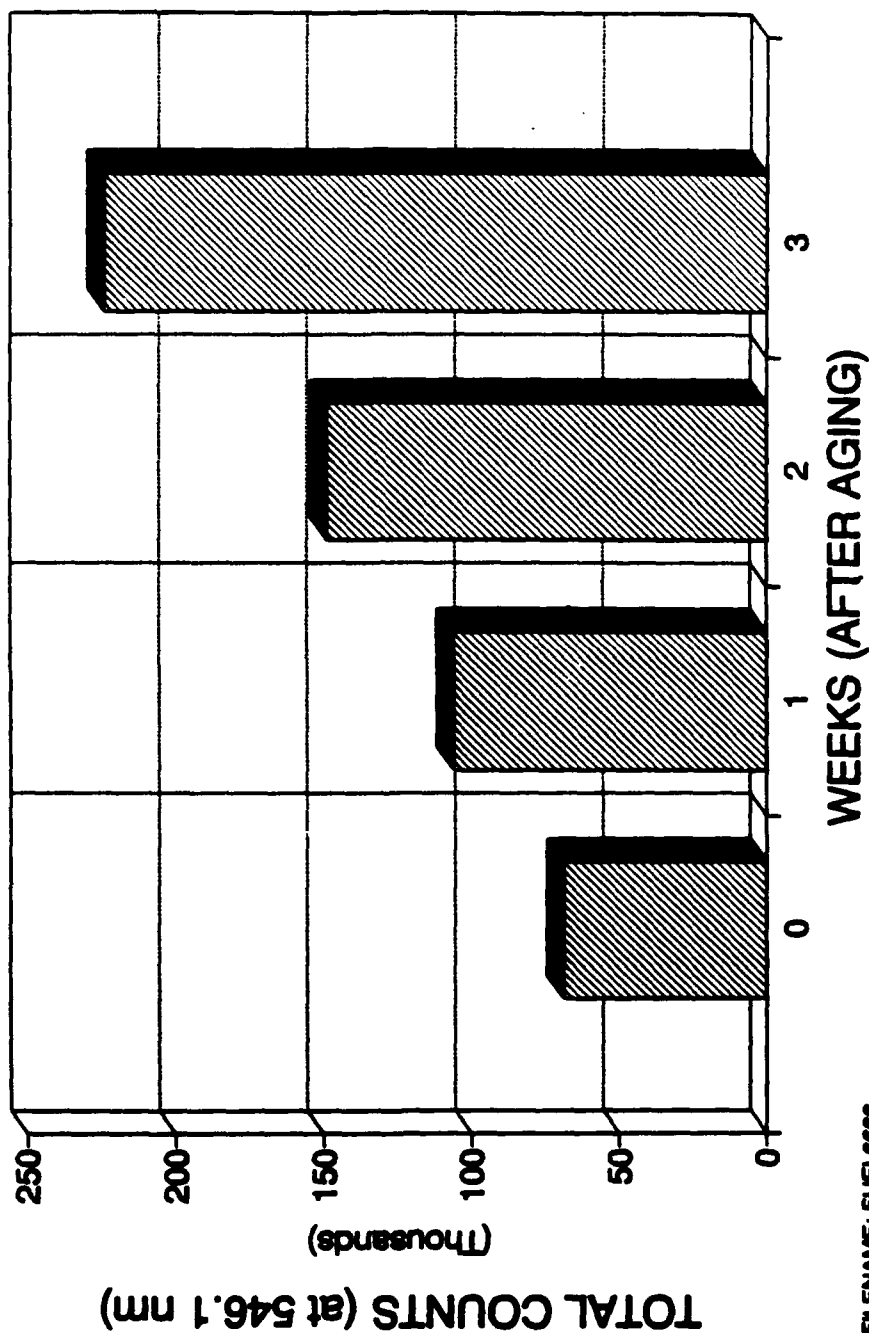


Figure 9. The effect of sample aging on the fluorescence intensity of soluble gums in surrogate JP-8, Fuel 1701

**LIF FL-1701-F 488/546.1
INSOLUBLE GUMS DISSOLVED IN TAM**

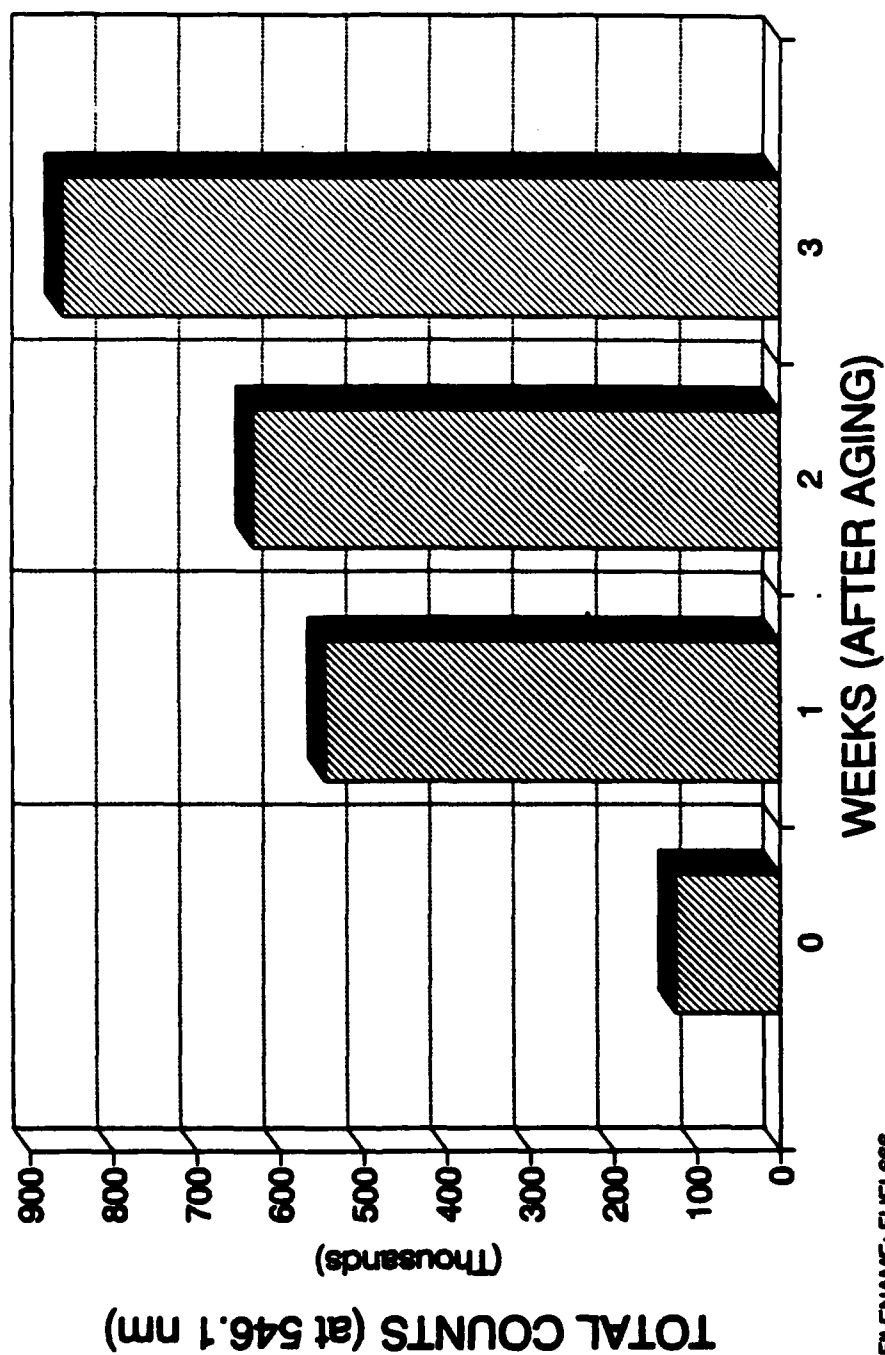


Figure 10. The effect of sample aging on the fluorescence intensity of insoluble gums from surrogate JP-8, Fuel 1701, dissolved in TAM

The results of the aging experiment suggest one of two possible explanations. Either the molecular structure of the gum changes with age, or gum formation continues in the fuel sample. The former seems to be the most probable elucidation because the effect of aging on LIF intensity is also observed in the insoluble gums that were dissolved in TAM. Gum formation is not expected to continue in TAM because TAM is a relatively inert solvent.

Fluorescence Quenching

It is well known that molecular oxygen is a particularly efficient fluorescence quenching agent. The ease with which energy is transferred from excited organic molecules to oxygen is due to the fact that molecular oxygen has a low lying $^1\Delta$ energy level that can absorb significant amounts of electronic energy. In the present study, it was important to investigate the possibility of fluorescence quenching because the test fuels were stressed under conditions of high oxygen pressure. In other words, the oxidatively stressed fuel samples could have been supersaturated with oxygen when the LIF measurements were made. The oxygen solubility measurements indicated that the stressed fuel samples contained at least 50 ppm of oxygen under atmospheric conditions. If fluorescence quenching was important, and the oxygen concentration was initially much higher than the equilibrium value of about 50 ppm, the LIF intensity would be expected to increase with time as the excess oxygen disappeared from the fuel sample.

To determine the importance of oxygen in fluorescence quenching, a relatively oxygen free fuel sample containing gum was prepared by purging the sample inside a cuvette with nitrogen to remove dissolved oxygen. The nitrogen was dispersed into the stressed Fuel 1701 for about 15 minutes and then the cuvette was capped to prevent contamination of the sample with oxygen from the air. In a similar way, a second sample of the same stressed Fuel 1701 was prepared by dispersing pure oxygen into the cuvette. Dispersion of the gases into the stressed fuel sample was performed by passing O_2 or N_2 through a #ES-10 needle in the sample cuvette. Both of the gases, O_2 and N_2 , were of research grade quality. The results of the LIF measurements did not show a significant difference in the fluorescence intensities from the two samples. It was concluded that oxygen quenching does not affect the LIF measurement of gums in jet fuels.

Responsivity

The term "responsivity" is used to describe in relative units, the fluorescence intensity that is emitted per unit of gum concentration in the test fuels. If fluorescence intensity is

expressed in counts at 546.1 nm, and gum concentration in mg/dL, the units of responsivity are counts/(mg/dL). Ideally, the responsivity of all the test fuels would be the same, irrespective of the fuels origin and composition. The results of this study show that the responsivities of the test fuels varied quite substantially. Responsivities for the various fuels were calculated from the LIF data presented in Table 3. The expression used to calculate the responsivity, R , was,

$$R = \frac{I_s - I_c}{[gum]} \quad (8)$$

where I_s is the intensity at 546.1 nm in relative LIF units (counts) for the stressed fuel, I_c is the intensity in relative LIF units (counts) for the control or neat fuel, and $[gum]$ is the concentration of gum in units of mg/dL.

For most of the test fuels in Table 3, the data are based on only one or two LIF measurements of gum, but for a few of the fuels, namely Fuel 1701 and 1791, LIF measurements were made on several gum samples. Responsivities of the test fuels were first calculated using all available data for each fuel in Table 3. Then an average value of the responsivity was obtained for each test fuel. Figure 11 shows the effect of the fuel oxidation rate (see Table 2) on the responsivity of the test fuels examined. Despite the wide variation in the responsivities of the test fuels, there seems to be some correlation with the rate of fuel oxidation. Figure 11 shows that the responsivities are much greater for the fuels that oxidize very slowly or have indefinite induction periods (no breakpoint). In contrast, the fuels that formed gums in the relatively short term during the post-induction time of the oxidative stress, give responsivities that are much lower and exhibit less variability.

The effect of oxidation rate on responsivity shown in Figure 11 may be explained, at least in part, by the effect of gum aging discussed above. The gums that form in fuels with low oxidation rates spend a much longer time in the oxidation bomb than those that are formed rapidly. This longer term exposure to high temperature seems to cause increased aging of gums, especially those that form early in the oxidative stress period. Because aging causes a significant increase in the fluorescence intensity of stressed fuels, it basically increases the responsivity of soluble gums in the fuel. The results of this work indicate that gums undergo significant changes in molecular structure well after their initial formation. Laser-induced fluorescence may be a useful method of monitoring the chemical changes that

Table 3. LIF Measurements

Fuel Sample	Gum Content (mg/dL)	Integration time per scan (msec)	Signal Intensity at 546.1 nm	Cal. Factor	Relative Intensity LIF units
1701	0.0	30	5,345	2.032	10,861
1701	0.2	30	5,856	2.032	11,899
1701	7.0	30	8,627	2.032	17,530
1701	15.0	30	19,034	2.032	38,677
1701	57.4	30	121,260	2.032	246,400
1701	3.9	30	7,151	2.219	15,868
1701	8.6	30	7,569	2.219	16,796
1701	5.9	30	7,721	2.219	17,133
1701	7.5	30	10,536	2.354	24,802
1701	27.3	30	19,969	2.354	47,007
1701	48.2	30	67,368	2.354	158,584
1701	56.3	30	102,960	2.354	242,368
1702	0.0	300	20,135	0.903	181,895
1702	15.1	300	80,962	0.903	73,141
1703	0.0	30	24,537	1.061	26,034
1703	5.8	30	56,627	1.061	60,081
1704	0.0	30	9,374	1.007	9,440
1704	2.7	30	63,135	1.007	63,577
1705	0.0	300	15,118	1.271	15,402
1705	6.2	300	111,467	1.271	141,675
1722	0.0	300	13,202	1.344	17,743
1722	22.8	300	29,979	1.344	40,292
1791	0.0	300	47,374	1.838	87,073
1791	29.2	300	200,850	1.838	369,162
1791	33.4	300	170,695	1.838	313,737
1791	46.8	300	268,341	1.838	493,211
1791	72.6	300	257,469	1.838	473,228
1791	77.6	300	268,416	1.838	493,349
1791	20.6	300	124,055	2.186	271,282
1791	46.9	300	146,094	2.186	319,361
1791	57.3	300	167,356	2.186	365,840
1791	89.7	300	182,646	2.186	399,264
1791	102.0	300	194,062	2.217	430,138
1791	201.0	300	181,036	2.217	402,596
1792	0.0	30	25,251	1.6038	40,497
1792	59	30	221,648	1.6038	355,479
1792	57	30	224,098	1.6038	359,408

Table 3. LIF Measurements (Continued)					
Fuel Sample	Gum Content (mg/dL)	Integration time per scan (msec)	Signal Intensity at 546.1 nm	Cal. Factor	Relative Intensity LIF units
1801	1	300	238,007	1.6038	381,715
1801	100	300	118,038	1.6038	189,309
1801	17	300	67,805	1.6038	108,745
1802	0.0	30	27,169	1.626	44,184
1802	2.0	30	65,536	1.626	106,579
1802	1.8	30	57,150	1.626	92,941
1823	0.0	30	52,843	1.6562	87,519
1823	135	30	138,892	1.6562	230,033
1824	0.0	300	68,163	1.6562	112,891
1824	0.9	300	78,786	1.6562	130,485
1824	45.4	30	9,660	1.6236	157,096
1825	1.2	30	121,572	1.656	201,323
1825	198	30	70,471	1.656	116,700

occur in gums. This could be important because it may be the chemical changes in gums that determine if they will produce deposits in hot sections of a jet engine fuel system.

Linearity

An important task in evaluating the use of LIF in measuring soluble gums was to determine the effect of soluble gum concentration on the fluorescence intensity. Preliminary experiments on linearity were performed using a dilution method. In this procedure, an LIF intensity measurement at 546 nm was first made on the stressed fuel sample which contained a known amount of gum. Subsequent LIF measurements were made on fuel samples that were produced by diluting the original sample with neat fuel. Figure 12 shows a typical plot of LIF intensity versus gum concentration in the fuel. The results show that the LIF intensity

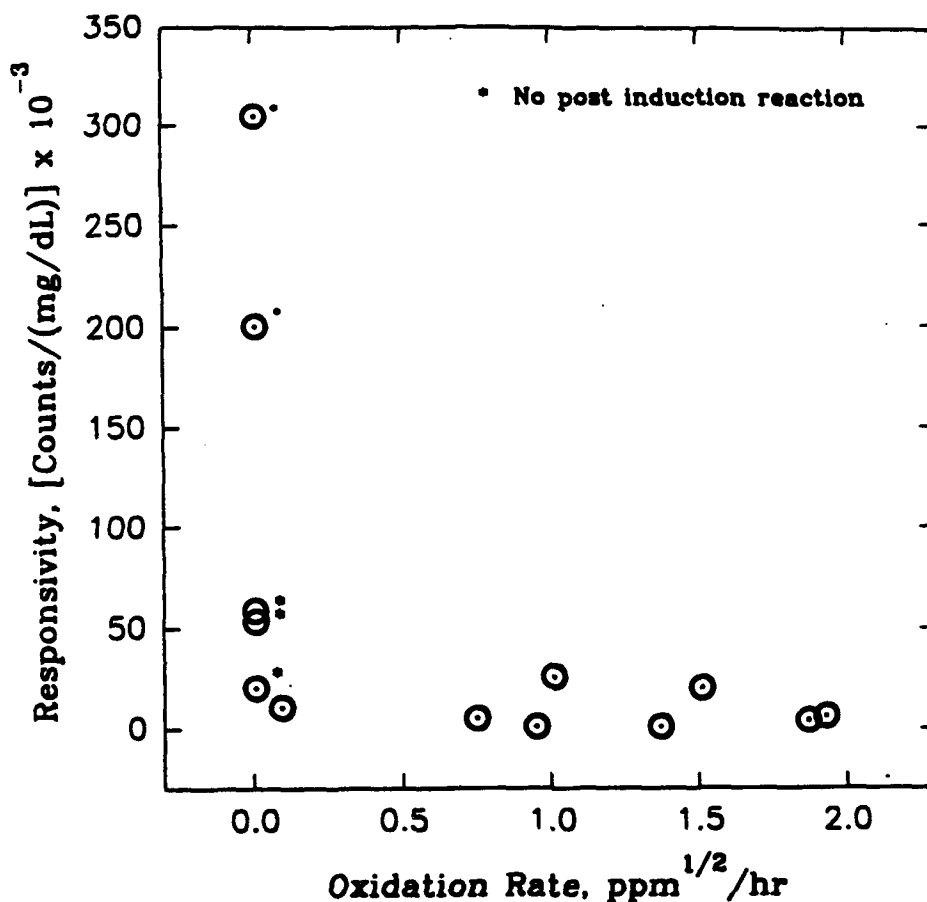


Figure 11. The effect of fuel oxidation rate on the LIF signal responsivity to gum concentration.

is directly proportional to the gum concentration in the fuel. Similar plots, made using gum samples from all the other test fuels gave equally linear relationships between gum concentration and fluorescence intensity.

The dilution method of determining linearity did not preclude possibility that some other fluorescent material could be formed by oxidative stressing and that other fluorescent material would not be representative of gum concentration if it was formed at a different rate than the bulk of the gum measured by D 381. For example, another fluorescent material might form very early in the oxidation reaction and then cease to form further while the bulk of the gum is produced. In that case the plot would show an abrupt increase in the LIF intensity followed by a relatively low gradient in the fluorescence intensity versus gum-concentration curve.

FL-1722-F 174hours/100 C/100 psig O2
(488/OG530/IF/300msec/100scans/100mW)

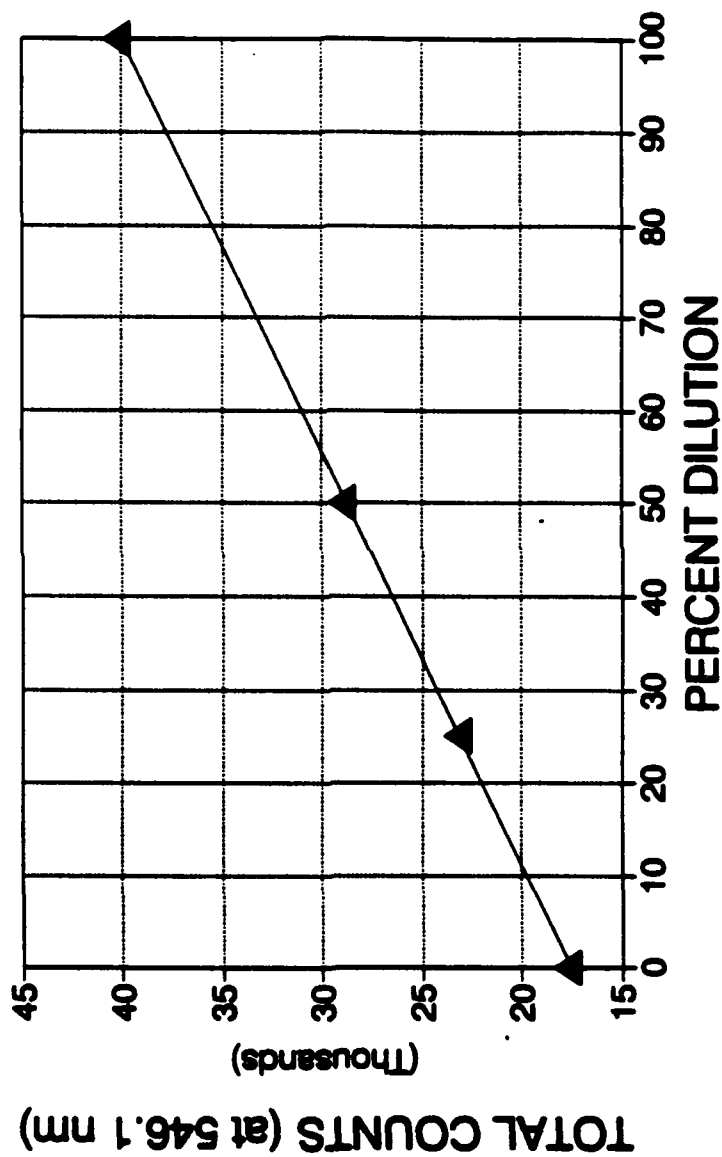


Figure 12. The effect of gum concentration on LIF intensity. Gum concentration was varied by diluting a sample of the stressed Fuel 1722 with the neat Fuel 1722.

To further examine the linearity question, Fuels 1701 and 1791 were each stressed for different periods of time to produce several samples containing different concentrations of soluble gum in the stressed fuel. LIF measurements were made on each of the stressed fuel samples and the results were plotted versus the concentration of soluble gum as measured by the D 381 steam jet method. Fuels 1701 and 1791 were selected for this study because they formed gums relatively fast and the neat fuels (controls) gave relatively low LIF intensity compared to the corresponding stressed fuel samples. The results of these measurements are shown in Figures 13 and 14.

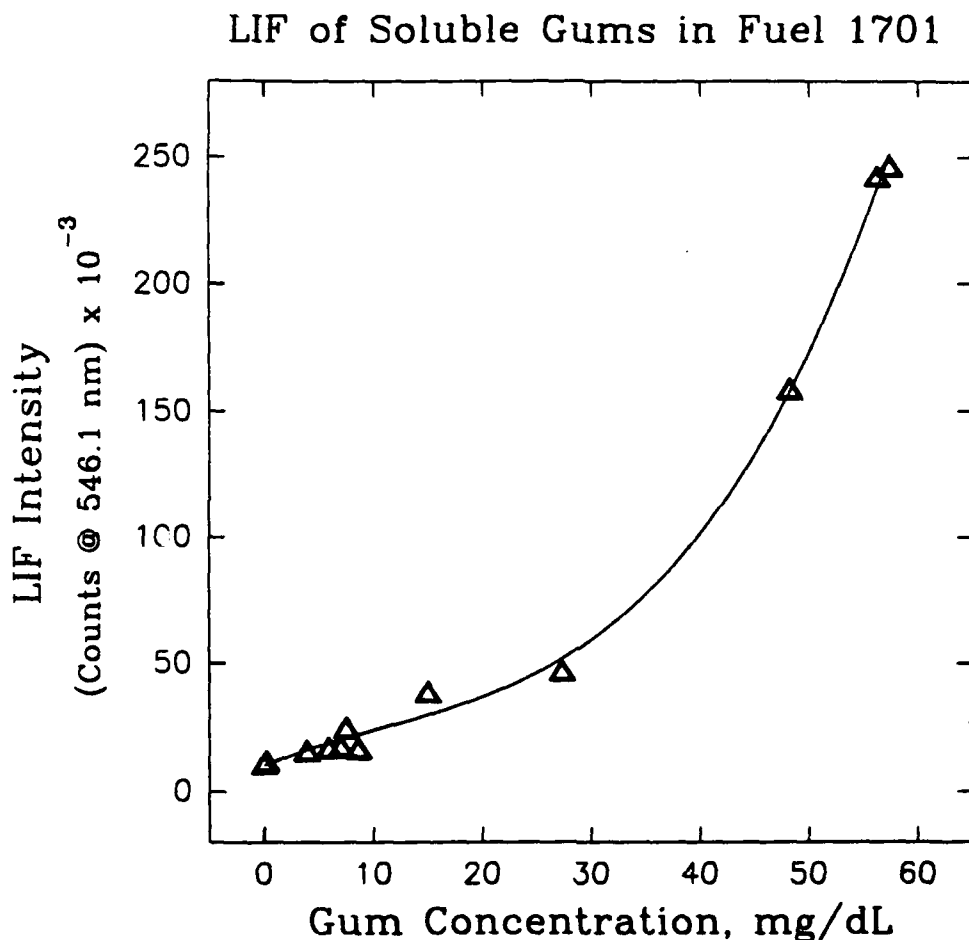


Figure 13. The effect of gum concentration on LIF intensity.
Note each point represents an individual oxidatively stressed sample of surrogate JP-8, Fuel 1701.

Figure 13 shows the dependence of the LIF intensity on gum concentration for the surrogate JP-8, Fuel 1701. The results show a monotonic increase in the LIF intensity with

rising gum concentration. It is encouraging in that there appears to be a reasonable correlation of LIF intensity with gum concentration for Fuel 1701. However, the upward curvature of the dependence is unexplained at present and can only be speculated upon. The curvature is not caused by an optical effect such as optical thickness developing as gum concentration is increased. LIF measurements were made using the dilution method starting with the fuel sample having the highest gum concentration (57.4 mg/dL) and the LIF intensity decreased linearly as the sample was diluted with neat fuel.

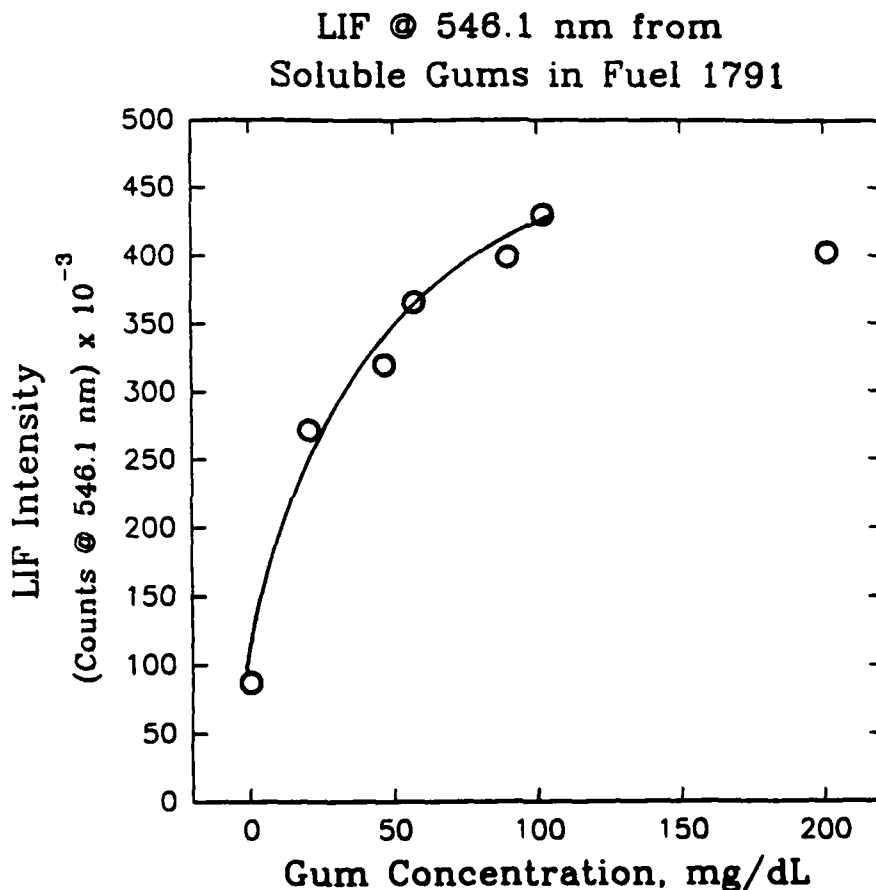


Figure 14. The effect of gum concentration on LIF intensity.
Note, each point represents an individual oxidatively stressed sample of JP-8X, Fuel 1791.

One possible explanation for this behavior is that gums of different molecular structures accumulate in the fuel at different rates as the fuel is oxidatively stressed. If the gums produced from the various fuel components have different responsivities, that could account for a change in the gross responsivity of the gums as the time for oxidative stressing

was increased. The problem with this argument is that a smooth curve such as that shown in Figure 13 would be highly improbable unless there was a strong correlation between the rates of gum formation in fuel components and their responsivities to LIF. Such a correlation is not apparent from the test fuel data in the present study, and there were no data acquired on pure compounds.

In light of the gum aging results presented earlier, it appears more probable that gum aging could account for the upward curvature of the LIF intensity versus gum concentration plot shown in Figure 13. The greater the duration of the oxidative stressing, the longer the gum formed early in the stressing period would have to be exposed to the relatively high temperature (100 °C) in the oxidation bomb. Since the LIF responsivity increases with gum aging, this seems to be a cogent explanation of the upward curvature seen in Figure 13.

Figure 14 shows the dependence of LIF intensity on gum concentration in JP-8X, Fuel 1791. For Fuel 1791, the dependence of LIF intensity on gum concentration seems to exhibit a slight downward curvature for gum concentrations ranging from 0 to about 100 mg/dL; beyond 100 mg/dL there was only one data point which indicates a flattening out in the LIF response. If the control data point is excluded from Figure 14, the curve shows relatively good linearity in the 12- to 100-mg/dL range. Either way, these results show promise in that there appears to be a correlation between the LIF intensity and the gum concentration. The difference in the dependencies of LIF intensity on gum concentration between Fuels 1701 and 1791 is unexplained other than it may have something to do with the fact that Fuel 1701 is a surrogate JP-8 while Fuel 1791 is an authentic JP-8X jet fuel.

LIF of Additives

A preliminary examination of the fluorescent properties of fuel additives was undertaken to determine if there would be an interference with the LIF measurement of gums in Jet fuels. Six additives, five liquid and one crystalline, including antioxidants, dispersants, detergents, and stabilizers were investigated.

The liquid additives were dissolved in the neat fuel 1701-F (surrogate JP-8) in concentrations of one drop of additive per 3 mL of fuel. For the crystalline additive, one small flake (≈ 1 mg) was dissolved in 3 mL of fuel. In these proportions the dissolved samples visually appeared clear, except for #2729 which was a light purple, and #2786 which was slightly yellow.

The LIF measurements were made in the usual manner using 488-nm light from an argon ion laser. Table 4 shows the results of the LIF intensity measurements at 546.1 nm. Complete spectral curves were digitally recorded for future reference.

The results in Table 4 indicate that some of the additives may be fluorescent in the concentration levels as measured. However, the concentrations shown in Table 4 are much higher than the 500-ppm limit used in most additive/fuel preparations. Most of the additives shown in Table 4 are used in concentrations less than 50 ppm so their fluorescence would not be expected to interfere with the fluorescence from gums.

TABLE 4. Laser-Induced-Fluorescence Intensity at 546.1 nm for Various Additives. Note That the Blank (neat fuel 1701-F) Was Approximately 18,050 Counts Which Should Be Subtracted from the Intensity Levels Before Direct Comparisons are Made.			
Sample Description	Approximate Concentration (ppm)	Fluorescence Intensity (counts)	Intensity Minus Blank Intensity (counts)
Neat 1701 (Blank)	10,000	18,050	0
Detergent 2729	10,000	25,172	7,122
Antioxidant/ Dispersant 2786	10,000	48,312	30,262
Detergent/ Dispersant 2744	10,000	27,567	9,517
Stabilizer 2748	10,000	52,095	34,045
Dispersant 2738	10,000	106,672	88,622
Antioxidant 29	300	19,112	1,062

In addition to the LIF measurements with the argon ion laser, the additives were also illuminated with 325-nm ultraviolet light from an He/Cd laser. The additives were essentially non-fluorescent except for samples 2748 and 2738 which emitted a weak green fluorescence. For these measurements, only visual observations were made of the fluorescence. The results further substantiate that the additive should not interfere with the fluorescence from gums.

CONCLUSIONS

The LIF spectra of the gums from the various test fuels were similar in that they occurred within the same spectral window (500 to 750 nm). However, there were variations in the half intensity widths of the spectra that should be addressed in future attempts to measure the fluorescence intensity of gums. An argon-ion laser was found to be a good excitation source for LIF of gums in jet fuels. Excitation sources in the ultraviolet at 325 nm and the red at 635.1 nm were not effective in the LIF detection of gums in jet fuels.

The results indicate that there is a correlation between LIF and the gum content of jet fuels. However, the LIF intensity is not a simple linear function of gum concentration. In view of the fact that a detailed study was performed on only two of the test fuels, the results on the effect of gum concentration on LIF intensity are inconclusive. In other words, it is not certain that the correlation function for the dependence of LIF intensity on gum concentration is the same for all jet fuels. Among the test fuels examined, two of the fuels showed a negative correlation between LIF intensity and gum concentration. However, it was concluded that those fuels, which gave negative correlations, contained fluorophores that interfered with the fluorescence from gums.

The present study indicates that gum aging has a significant influence on the relationship between LIF intensity and gum concentration. This result indicates that gums undergo significant changes in molecular structure for a period well after their inception.

The responsivity of LIF to gums varied with fuel specification and composition. It appeared to depend partly on the rate at which gums were formed in the test fuels. Extreme variations in responsivity appeared to be related to gum aging. It is concluded that gums undergo significant changes in chemical structure for some time after their initial formation. This problem of changing responsivity is a factor that complicates the use of LIF in making an absolute measurement of soluble gums in jet fuels.

Fluorescence quenching by molecular oxygen was found not to interfere with the LIF detection of gums in jet fuels. Preliminary LIF measurements show relatively weak fluorescence from fuel additives. It is concluded that fluorescence from fuel additives will not interfere with the LIF detection of gums in jet fuels.

This study has revealed several effects, such as gum aging and the interference of other fluorophores with gum-fluorescence, which require further investigation before LIF is to be considered a quantitative technique for measuring gums in jet fuels. However, this study has shown that the formation of gums in jet fuels is detectable by LIF. The results of this study show that gum formation in some fuels correlates strongly with LIF while for other fuels the results are ambiguous. In other words, if the test fuel is selected carefully, there is a high probability that gum formation will correlate with LIF. On that basis, the present study indicates that LIF could become a very useful research technique for making spatially-resolved nonintrusive qualitative-measurements of gums in experiments on jet fuel stability and deposit formation.

RECOMMENDATIONS

- To continue this program, the objective should be to gain a more basic understanding of the effects of gum concentration, aging, etc., on LIF spectra and fluorescence intensity.
- Fuel stressing should be performed at higher temperatures in a flow tube. Because of the problems of gum aging a strict schedule should be imposed on the attainment of gum samples, D 381 gum analysis, and the measurement of LIF.
- The gum aging phenomenon should be examined in more detail. The effects of storage conditions such as light, sample volume, temperature, etc., on $d(\text{LIF})/dt$ should be measured.
- Measurements should be made on the effects of additives on LIF of stressed fuel. For example, $d(\text{LIF})/dt$ should remain constant while the additive remains effective in preventing the formation of gum in the stressed fuel.
- Pure compounds such as dodecane and tetralin should be included in the test fuel matrix. This would provide a better understanding of the gum spectra, aging, and the effect of gum concentration on LIF intensity. The pure compounds and the test fuels included should be clay filtered to remove all fluorophores and oxidation products that

might interfere with the LIF measurements. This may be particularly effective in the coal derived fuel where it appears that fluorophores are more prevalent.

SUGGESTED NEW WORK

For follow-on work in the LIF detection of gums, it is suggested that experiments be performed at higher temperatures, i.e., more realistic temperatures in terms of thermal stability and deposit formation. Measurements should be made on the rates of formation of peroxides and gums in a flow tube at higher temperatures ($> 200^{\circ}\text{C}$) using the test fuels examined in the present study. In this way gum samples can be obtained quickly so scheduling of the D 381 analysis and the LIF measurements can be made more consistently.

In recent studies on fuel oxidation and thermal stability, fuels that oxidize rapidly tend to have a greater thermal stability than fuels that are highly resistant to oxidation. This appears to have something to do with the precursors that are formed during the initial oxidation of the fuel. These observations suggest new studies to determine the effects of prestressing on the thermal stability of test fuels examined in the present study. Since one theory is that oxidation inhibitors actually contribute to the formation of deposits, it would also be important to examine the effects of additives on the oxidation products of prestressing and the deposits that would form at high temperatures. Both the neat fuel and the stressed fuel would be analyzed for heteroatom and olefinic compounds. The analysis would be performed with mass spectroscopy and gas chromatography equipped with heteroatom specific detectors. Laser-induced fluorescence could be a way to monitor the formation of gums during prestressing, but, more importantly, it may also indicate changes in the molecular structure of gums that effect deposit formation.

In the present study the LIF measurements were made with a continuous-wave laser. An attempt was made to examine oxidatively stressed fuel samples with pulsed laser excitation, but a conclusive study was not within the scope of the present program. The reason for examining gums with pulsed excitation is that there may be discernable variations in the fluorescent lifetimes of gums and other fluorescent materials in the fuel. This could significantly improve the sensitivity of the LIF technique by reducing background fluorescence and provide additional parameters which could be correlated with gum formation.

Follow-on Instrumentation

Instrumentation based on the laser-induced fluorescence technique has been constructed under another project for the inspection of polymer degradation.⁽¹⁹⁻²²⁾ In that case utilizing integrated fluorescence allowed the use of a small air-cooled argon-ion laser for the excitation source and an inexpensive photomultiplier tube/glass filter combination for the detector. (Total cost of the equipment was less than \$15,000.) A similar system could be constructed for measurements on degraded jet fuel.⁽²³⁾

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